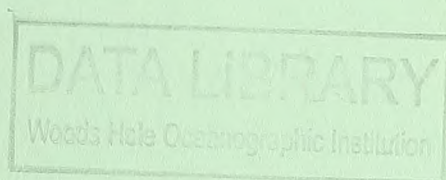


Chemical Oceanographic Research:

Present Status and Future Direction



OFFICE OF NAVAL RESEARCH
Arlington, Virginia

Approved for public release; distribution unlimited.

6C
58
.C4
1972

Chemical Oceanographic Research:

Present Status and Future Direction

*Deliberations of a workshop held at Naval Postgraduate
School, Monterey, California, December 11-15, 1972*

*Dr. Neil R. Andersen, Convener, Ocean Science and Technology
Division, Office of Naval Research, Arlington, Va.*



Sponsored by
Office of Naval Research
Arlington, Virginia

PREFACE

Oceanography can be portrayed as a description of the sea as an environment, and as the study of all processes taking place within this environment and at its boundaries. Oceanography thus utilizes a variety of scientific disciplines, and its division into separate fields of study, such as chemistry and biology, is somewhat artificial. Nevertheless, a growing awareness of specific chemical problems and recent trends in studying the chemistry of the marine environment provides a basis for identifying chemical oceanography as a discrete programmatic area. This recognition is underscored by the fact that all branches of oceanography in some way depend on chemical information and techniques.

Traditionally, chemical oceanography has been almost completely descriptive, with emphasis on analytical chemistry. In the majority of cases, these studies have been solely directed at identifying water masses to gain insight into their movement and mixing, and at assisting biological investigations, such as productivity studies. More recently, however, the chemical oceanographer has been seeking to elucidate the entire spectrum of physical and chemical processes responsible not only for the composition of the ocean itself but also for the reactions occurring at the various interfaces (i.e. air-sea, sediment- and land-sea, and suspended material-sea). These considerations embrace the occurrence and distribution of the elements in the ocean and the types of reactions that occur between the various chemical species in solution, as well as the rates and mechanisms of supply and removal of each oceanic component (i.e., the routes and reservoirs).

To explain the results of chemical studies, it is often necessary to consider circulation and mixing patterns and also interactions between the various phases present. Thus, chemical investigations of basic processes in the ocean environment can yield a better understanding of the chemical processes, and the results can elucidate physical processes of the ocean, such as water mass movement and mixing. As in the past, chemical oceanographic research will provide support and assistance in the understanding and solution of problems that mainly concern disciplines other than physical oceanography, such as marine biology and geology. Moreover, conducting a research program in a manner that addresses fundamental processes in the marine environment will reduce the constant redirection and disruption of well-planned research efforts arising from the pressures of newly recognized or socially active

problems (e.g. pollution) that will continually arise. In general, the results of basic research will have direct applicability to such problems.

The major operating area of the Navy is the open ocean. However, ports and harbors with a wide range of marine environmental characteristics are also used extensively. To operate effectively, the Navy must possess a substantial knowledge of this marine environment; with this knowledge the degree of operational effectiveness obtained can be directly related to the understanding of all the factors that make the oceans and their properties what they are. It is for this reason that the Office of Naval Research supports a diverse research program in the ocean sciences. Inasmuch as chemical oceanography occupies a central role in the understanding of the multifaceted marine environment, chemical oceanographic research forms a part of this Ocean Sciences Program. The research provides insight into the processes and mechanisms that determine the chemical character of the sea. Therefore, it is directly applicable to solving specific problems of Navy relevance, such as the corrosion and deterioration of materials in the marine environment; the monitoring, assessment, and possible control of pollutants in the sea; the interchange of materials across the air-sea and sea-bottom boundaries; the effect of chemical processes on the properties of sound transmission, absorption, and scattering in the marine environment; and the use of tracers for the identification of water masses in studying ocean circulation and mixing mechanisms. All these problem areas share a common basis in chemistry.

Unfortunately, most of the basic marine chemical processes, their controls, mechanisms, alterations by outside influences (e.g. pressure), and their effects upon man's utilization of the ocean, are not well understood. The number of organic compounds in the sea far exceeds that of all inorganic species combined, yet little is known of their involvement in trace-element chemistries. Few laboratories pursue the qualitative or quantitative assays of organics in the marine environment. We now possess only an extremely crude understanding of the chemical basis and effects of sound attenuation in the ocean. We know virtually nothing of the basic mechanisms and interrelationships of the chemical and bacteriological processes resulting in the corrosion of material in the marine environment, or the effects of antifouling material (e.g., copper) on a semienclosed body of water supporting heavy ship traffic. These are but a few examples. The objective of the research supported by the Navy in chemical oceanography is to understand the controls and mechanisms maintaining the chemical characteristics of the ocean environments and to elucidate the properties of marine equilibria. That understanding will then be applied to solving problems of naval relevance.

The attainment of the aforementioned goal is synonymous with determinations of the present status and future direction of the field of

chemical oceanography. To determine where chemical oceanography stands at the present time and what are the pressing problems that should be attacked during the next several years (i.e., the direction of the field), a group, comprising prominent American chemical oceanographers, assembled at the Naval Postgraduate School, in Monterey, California, December 11-15, 1972. Four days of deliberations and discussions were conducted in three major areas of concern: (A) Processes and Mechanisms Governing the Inorganic Composition of Seawater, (B) Chemical Fluxes Through the Marine Environment, Including Air-Sea and Sediment-Sea Exchanges, and (C) Impact of Life Processes on the Chemistry of the Ocean. The specific objectives of this conference were (1) to promote the exchange of information, especially among ONR-supported scientists; (2) to promote any cooperative research; and (3) to assess the future areas of investigation in chemical oceanography and thereby make recommendations for the future direction of research in this field generally, and thereby the ONR Program, specifically. The first two of these objectives were accomplished during the gathering. The third objective, the results of the considered opinions of the participants of the meeting, are contained in the subsequent text. This discussion not only provides insight into the extent of contemporary understanding of the chemistry of the ocean, but also addresses specific problem areas requiring research to enhance this understanding.

Neil R. Andersen
Workshop Convener
Washington, D.C.
February, 1973

CONTENTS

Preface.....	iii
Executive Summary	1

Session A

Processes and Mechanisms Governing the Inorganic Composition of Seawater *Dr. Frank J. Millero, Discussion Leader*

INTRODUCTION	5
SEAWATER AS A MEDIUM	7
The Chemical Composition of Seawater.....	7
The Physical and Chemical Properties of Seawater.....	12
Chemical Interactions Among the Major Components.....	13
Measurement and Prediction of the Properties of Solutes in Seawater.....	15
MINOR ELEMENTS	16
Homogeneous Reactions	17
Heterogeneous Reactions	18
Air-Sea Interface	21
Analytical Studies	21
ROLE OF ESTUARIES IN MODIFYING SEAWATER COMPOSITION.....	23
PARTICULATE MATTER.....	25
ROLE OF BOTTOM DEPOSITS IN MODIFYING SEAWATER COMPOSITION	26
NUMERICAL MODELS IN CHEMICAL OCEANOGRAPHY	27

Session B

Chemical Fluxes Through the Marine Environment, Including Air-Sea and Sediment-Sea Exchanges *Dr. Edward D. Goldberg, Discussion Leader*

INTRODUCTION	31
--------------------	----

PLUTONIUM CHEMISTRY OF THE OCEAN	33
Present Conditions in the Ocean.....	33
Chemical and Radioactive Properties	35
FACTORS GOVERNING THE COMPOSITION OF SEAWATER BELOW THE POLAR ICE COVER.....	35
PARTICULATE FLUXES IN THE OCEAN.....	36
DETERMINATION OF THE EXCHANGE OF GASES BETWEEN THE ATMOSPHERE AND THE SEA.....	39
DETERMINATION OF THE FLUXES OF ORGANIC MATTER IN THE MARINE ENVIRONMENT.....	41
DETERMINATION OF THE FLUXES OF NOBLE GASES, INCLUDING RADON, AND LOW-MOLECULAR-WEIGHT ORGANIC GASES FROM THE SEDIMENTS INTO THE OVERLYING WATERS.....	42

Session C

Impact of Life Processes

on the Chemistry of the Ocean

Dr. Francis A. Richards, Discussion Leader

INTRODUCTION	45
IMPACT OF LIFE PROCESSES ON THE MAJOR CONSTITUENTS.....	47
IMPACT OF LIFE PROCESSES ON HEAVY METALS.....	49
Contemporary State of Knowledge.....	49
Processes, Rates, and Mechanisms	50
Modeling	52
Future Efforts	52
IMPACT OF ORGANISMS ON MARINE ORGANIC CHEMISTRY.....	52
LIFE PROCESSES AND NUTRIENT SUBSTANCES.....	55
Nutrients and Dissolved Gases	57

Synthetic Organic Materials	59
HYDROCARBONS IN THE MARINE ENVIRONMENT.....	61
Occurrence, Formation, and Degradation	61
Hydrocarbon Gases	61
REDOX POTENTIAL, pH, AND ALKALINITY	62
Redox Potential	62
pH	63
Alkalinity	65
IMPACT OF LIFE PROCESSES ON RADIOACTIVE AND STABLE NUCLIDES.....	66
REFERENCES	67
PARTICIPANTS.....	79

EXECUTIVE SUMMARY

The following discussions consider in varying detail the present status of knowledge in chemical oceanography and the various problem areas that merit research support during the next several years. The purpose of these comments is to summarize the collective recommendations of the workshop participants, and not to preempt background material in the succeeding sections.

Because residence times of the chemical constituents of seawater are much shorter than the age of the oceans, chemical processes removing these constituents must occur continuously. Although there are many possible reactions, the sites where most reactions occur are essentially unknown. Two locations for many of the reactions, the continental margins and the photic zone, are probably highly important and have been little studied as areas where the mechanisms that control the major constituents of seawater operate. These areas should be studied in detail, using new field techniques such as *in-situ* sensors. Their highly reactive amorphous phases should be characterized and experiments should be designed to elucidate their thermodynamics and kinetics. Both field and laboratory experiments should be carried out on the possible effects of organisms on major and trace-element constituents, as well as on the conventional nutrients and organic phases, and these experiments should be coupled with physical oceanographic and geochemical work on the same areas.

In addition to investigations at the geographical locations indicated above, identification of other sites where chemical processes are active is needed. For example, chemical reactions (e.g., adsorption), including their kinetics, need to be studied throughout the range of salinities encountered where river water mixes with seawater, taking into account seasonal changes. Specific consideration should be given to chemical speciation and the association of these species with inorganic and organic ligands.

More research needs to be conducted on the pressure-volume-temperature (P-V-T) relationships of seawater to provide a more reliable equation of state and to improve our understanding of the effect of pressure on chemical equilibria. Differences in data on the physical properties of seawater should be reconciled. Associated with this area of research, more work is needed on the kinetics and equilibria responsible for the properties of sound (e.g., absorption) in the marine environment. Research is also needed on the generation of gas bubbles (e.g.,

O₂, H₂S, and CH₄), their characterization and chemical composition in seawater, the diagenetic processes resulting in the formation of gases in the sediments, and their flux into the overlying water.

Variations in space and time of suspended matter in the ocean require further research as do processes occurring at the ocean bottom and the influence of sediments on the chemistry of the water column. Specifically, mechanisms and rates of *in situ* production and consumption of suspended material need to be determined both in the water column and at the bottom. The occurrence of trace elements in calcareous and silicious tests needs further elucidation, as do the rates of reaction (e.g., solution) of such tests. Similar studies on the hydrated metal oxides and particulate organic carbon are needed. The composition and flux of organic carbon and the preferential formation of minerals (e.g., high magnesium calcite over aragonite) are important research areas.

A host of organic compounds is dissolved in the sea, yet their composition, distribution, and ecological importance are unknown. An inventory of organic chemicals in the marine environment needs to be established, and their origin, age, composition, and fate need to be determined. Processes, mechanisms, and rates—both in rapid-turnover areas as well as low-productivity locations—need to be studied. For example, what is the role of organic matter in sedimentation, diagenesis, and air-sea interaction? What is the nature of the interaction between organic matter and the inorganic components of the ocean?

Many aspects of the influence of the ecosystem on chemical distributions are unknown, specifically with respect to heavy metals. Knowledge of the distributions, forms, and fate of these chemicals is presently inadequate to define their role in stimulation and control of the biosphere. Little is known of the synergism and antagonism of heavy metals in this system. The low levels of chemical constituents that control biological systems and the competitive nature of membrane transport sites require that low concentrations, both of nutrients and of antimetabolites (such as arsenate and trace metals), be considered simultaneously. Backleakage of nutrients and of organic metabolites significantly alters water chemistry; the rates of backleakage are important terms in the flux relations in any models constructed. Realtime rates of nutrient uptake are needed and the regulatory processes that control and determine the characteristics of nutrient fields need further investigation, especially for incorporation into models.

The marine environment is a dynamic system. Our degree of understanding of this system will be directly related to our understanding of chemical fluxes within it. Important questions concern how much material is being added to the present-day ocean from each of the various sources and how much is being removed to each of the various sinks. Do addition and removal rates change as functions of time? Information

on the injections of major and minor elements into the oceans, their speciation, and regional mesoscale air-sea transport studies of reactive and unreactive gases (e.g., the transfer coefficients), can be used to calculate time-dependent fluxes. This information can then serve as the basis for constructing three-dimensional models describing oceanic processes that in turn provide the foundation for predictions of oceanic conditions, predictions that, for operational needs such as those of the Navy, can be considered the ultimate goal of oceanographic research.

Two specific recommendations for future research were made: (1) the study of plutonium chemistry of the ocean, and (2) chemical processes occurring under and near ice. Plutonium is a toxic, radioactive, man-made element whose behavior in the marine environment is inadequately known. Only a few determinations have been made of its concentrations in seawater, in marine organisms, and sediments. The use of plutonium is expected to expand rapidly. Two of its nuclides, Pu-239 and Pu-238 are being used as fuels, and accidents have already released both of them into the environment. The chemical behavior of plutonium in the ocean cannot be extrapolated from what has been observed on land, making it essential that the marine chemistry of this element be understood.

The second specific research recommendation was to study the factors governing the composition of seawater below the polar ice cover. Neither the effects of freezing of seawater on the chemistry of the water-ice interface nor ice-related chemical processes are generally well understood. The intermittently ice-covered polar seas may be areas of strong air-sea gas exchange. The freezing process and biota unique to the ice-seawater system may impart chemical properties to this seawater that may be distinct from those of open-ocean regions.

The research recommended, discussed during the workshop, and summarized here was selected on the basis of immediate requirements in the field of chemical oceanography. However, as was pointed out in the Preface, the recommendations will also form the basis of a research program to be applied to solving diverse operational problems with which the Navy is faced. For example, in some regions the scattering of sound by biological populations in the upper layers can place practical limits on the operation of low-frequency (2-20 kHz) sonar. In recent years it has become clear that scattering strength varies over the oceans in accordance with some pattern. The pattern is apparently associated with variations in populations of marine organisms whose density and distributions closely depend on other links in the food chain, on mixing, thermal gradients, light, chemical nutrients, etc. A data base of volume reverberation measurements has been accumulated for the development of a prototype model for forecasting volume reverberation. Zones of

scattering strength stand out as identifiable regions of the ocean. Significant correlations between zooplankton distribution and volume reverberation are encouraging, but our understanding must be improved. More effort is needed in investigating the dynamic character of the interactions between biological populations of "natural hydrographic regions" and the chemical variability of their waters. Results of research in chemical oceanography, as recommended in this document, can have numerous applications in gaining this understanding of the chemical factors responsible for the seasonal and long-term changes in marine ecosystems and bioacoustical provinces of the ocean, and in providing a prediction capability. This is but one example of the many applications of results from basic research in chemical oceanography to the solving of operationally Navy-relevant problems.

The amount of published information in the field of chemical oceanography, like that in many other fields of science, has doubled every few years recently. Moreover, much information germane to problems of chemical oceanography is generated by parties in diverse fields, remote from the problems faced in chemical oceanography, and is published in journals or kept in files not readily accessible to oceanographers, except by occasional, coincidental contacts or discoveries. No concerted effort has been made to search out appropriate information, evaluate it, and present it to the oceanographic community. The lack of such an effort has an unknown, but possibly significant, impending effect on progress in chemical oceanography. Under the traditional system of financing oceanographic research, principally with the aim of collecting more data, the inefficiency of information gathering, synthesis, and transmittal to younger and future scientists is growing.

This situation should be remedied. It should be financially and scientifically sound to periodically free selected, experienced individuals from the burden of having to collect new data and sponsor them, for perhaps a year, for the purpose of collecting, synthesizing, and presenting scattered information in their field of expertise. Another possible solution is to have some junior investigators at each research institution for the purpose of gathering and assimilating information in support of existing programs.

Session A

Processes and Mechanisms Governing The Inorganic Composition of Seawater

Dr. Frank J. Millero, Discussion Leader

INTRODUCTION

The ocean is commonly considered a steady state system, at least with regard to the major dissolved constituents over long periods of geological time. Furthermore, it appears that throughout most of the ocean the ratios Na/Cl, K/Cl, SO_4/Cl , Mg/Cl and Br/Cl are constant within analytical precision (Lyman and Fleming, 1940; Culkin, 1965; Culkin and Cox, 1966; Riley and Tongudai, 1967; Riley and Chester, 1971). There is conflicting evidence regarding the variability of Sr/Cl, HCO_3/Cl , $\text{B(OH)}_3/\text{Cl}$ and F/Cl. The variations of Ca/Cl with depth have been well defined. Fluctuations arising from river runoff and freezing are locally significant, and may, such as in the Arctic, include vast geographical areas (see p. 35). The minor elements are potentially more variable in concentration and reactive in the marine environment; however, in most cases reliable analytical data and physical chemical understanding of these variations are lacking. The present status of our knowledge of the chemical composition of seawater and of chemical speciation, as well as needed research, were reviewed previously by Pytkowicz and Kester (1971).

The processes that control the major composition of seawater must be removal reactions, because the residence times of these elements are shorter than the age of the ocean. Although the equilibria models of Sillén (1961; 1965a,b; 1967a,b), Holland (1965), and MacKenzie and Garrels (1966a,b) have yielded reasonable suggestions as to how seawater attained its present major composition and how this composition is maintained, many questions exist concerning the mechanisms and processes that regulate the concentrations of all the major and minor constituents. Many questions pointed out by Broecker (1971), Chave and Smith (1972), and others concerning the effect of the circulation of the world's oceans and the effect of biochemical processes on the composition of seawater remain unanswered. For example, Pytkowicz

has shown that equilibrium models of the ocean may often not apply, in that for the carbon dioxide system, kinetic controls by organisms are more likely than controls by chemical equilibria. To test whether the ocean is in a steady state, or, if not, how the system is approaching equilibrium, it is necessary to identify the chemical reactions that regulate the concentration of each element and to determine the physical chemistry of each reaction.

Correct specific or generalized concentration-control reactions for the major constituents of seawater probably can be written. Our knowledge of the thermodynamics, the kinetics, and the environmental influences on these reactions varies considerably. Some of our ignorance is a result of the natural (biological or chemical) production of thermodynamically unstable phases or of extremely slow reactions.

We cannot state with certainty the concentrations of the minor constituents of seawater, let alone define the chemical and physical reactions that control the concentrations.

To understand the processes and mechanisms governing the inorganic composition, three major questions must be answered. What is the medium of seawater? What kinds of chemical reactions control the composition of seawater? Where do these chemical reactions occur?

In the following discussion we have attempted to focus on six major topics that should lead to a better understanding of the processes and mechanisms controlling the inorganic composition of seawater. These are (1) seawater as a medium; (2) minor elements; (3) the role of estuaries in modifying the composition of seawater; (4) particulate matter; (5) the role of bottom deposits in modifying the composition of seawater; and (6) numerical models in chemical oceanography.

Some important areas where information concerning the processes and mechanisms governing the inorganic composition of seawater is needed include the following (National Academy of Sciences, 1971a):

- Pollution of the environment. Since the ocean is the final reservoir for pollutants, we must have a better knowledge concerning the fate of present and potential pollutants. The introduction of radioactive wastes (such as plutonium) to the marine environment may present us with many new problems.

- Chemical products from the sea. Although it is not possible at present to recover economically trace constituents from seawater, further work may yield better methods than those presently being used.

- Desalination. With the increasing need for water, new techniques may become available.

By studying the chemical processes that control the composition of seawater under natural conditions (a dynamic chemical system) and obtaining an understanding of the inputs and outputs (the fluxes), much better estimates can be made for changes that will occur in the oceans.

Since the future of the earth is intimately related to the future of the oceans, it is important to understand the composition of seawater and how this composition affects the processes occurring in the oceans.

SEAWATER AS A MEDIUM

Some of the major questions facing chemical oceanography are: How did seawater reach its present composition? How does this composition affect processes that control the composition of minor components? Part of the answers are related to the questions, what is the medium of seawater? What are the chemical forms of the major components? What fluctuations occur? How are the physical and chemical properties of seawater related to the chemical composition? How does the medium of seawater influence various chemical processes occurring in the oceans? Although the answers to some of these questions have been found, many questions still remain and must be answered. In the following section some of the areas that have been studied, and some that need to be studied further are discussed briefly. This discussion will be divided into four major topics: the chemical composition of seawater, the physical and chemical properties of seawater, chemical interactions among the major components, and measurement and prediction of solutes in the medium of seawater.

The Chemical Composition of Seawater

Although we know the concentrations of the major components (Lyman and Fleming, 1940; Culkin, 1965; Riley and Chester, 1965; Pytkowicz and Kester, 1969 and 1971) (Table 1), little is known about the mechanisms regulating these concentrations in the oceans and where this regulation occurs.

From Table 2, it can be seen that thermodynamic and kinetic data on the concentration-controlling reactions for the major dissolved constituents of seawater are limited. Furthermore, organic processes are known to influence some of these reactions. To understand the mechanisms controlling the concentration of more than 99% of the dissolved matter in seawater, it is necessary to study many of the reactions in Table 2. This can be done through

1. Careful studies of pure systems in the laboratory
2. Careful studies of "carefully impure" systems in the laboratory
3. Careful studies of real oceanic situations with as many variables as possible controlled
4. Chemical and structural analysis of materials (notably aluminosilicates) supplied to the oceans from the land

TABLE 1
The Most Abundant Ions in Seawater*

Species	gm/Cl (%)†	1 Kgm of Seawater†	
		gms	Molality
Na ⁺	0.55556	10.763	0.48525
Mg ⁺²	0.06680	1.294	0.05519
Ca ⁺²	0.02125	0.412	0.01065
K ⁺	0.02060	0.399	0.01058
Sr ⁺²	0.00014	0.008	0.00009
Cl ⁻	0.99894	19.353	0.56579
SO ₄ ⁻²	0.14000	2.712	0.02927
HCO ₃	0.00735	0.142	0.00242
Br ⁻	0.00348	0.067	0.00084
B(OH) ₃	0.00132	0.026	0.00041
F ⁻	0.000067	0.001	0.00007
H ₂ O	—	964.823	—

*Values of g/kgm of seawater/chlorinity seawater; taken from Millero (1973a,b).

†For 35‰ salinity or 19.374‰ chlorinity seawater; taken from Millero (1973a,b).

5. Chemical and structural analysis of intermediate natural materials in the iron-sulfur and similar systems
6. Use of information and materials in 4 and 5 and experiments in 1-3.

Since the oceans have nearly a constant composition of constituents, reactions must be occurring nearly equally everywhere (unlikely) or at rates slower than mixing rates (likely). When we ask the question, "Where do these reactions take place?" we come up with several answers, and each answer raises a question. Consider the reactions listed in Table 2.

Reaction 1. About 10^{15} moles of CaCO_3 are precipitated in the oceans yearly. The majority of this precipitation in near-surface pelagic areas as a result of biological activity; lesser amounts are biologically precipitated on continental shelves and on coral reefs. Although the near-surface layers of the ocean are invariably super-saturated with CaCO_3 , there is little evidence for chemical precipitation of this compound. This problem is discussed by Chave and Seuss (1970) and Pytkowicz (1965). Another problem concerned with Reaction 1 is that

TABLE 2
Chemical Reactions Controlling the Concentration
of Major Constituents in Seawater

Reaction	Knowledge		
	Thermodynamic Data	Kinetic Data	Organic Influence
Dissolved—Solid Reactions:			
1. $\text{Ca}^{+2} + 2\text{HCO}_3^- \rightleftharpoons \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$	Much	Some	Much
2. $\text{Ca}^{+2} + \text{SO}_4^{-2} + 2\text{H}_2\text{O} \rightleftharpoons \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Much	Some	None (?)
3. $\text{Fe}^{+2} + \text{HS}^- + (\text{H}_2\text{O}) \rightleftharpoons \text{FeS} \cdot n\text{H}_2\text{O} + \text{H}^+$	Some	Some	Much
4. $\text{FeS} \cdot n\text{H}_2\text{O} + \text{H}_2\text{S} \rightleftharpoons \text{FeS}_2 + (\text{H}_2\text{O})$	Some	Some	Unknown
5. $\text{Na}^+ + \text{Cl}^- \rightleftharpoons \text{NaCl}$	Much	Much	None
6. $\left. \begin{array}{l} \text{K}^+ \\ \text{Mg}^{+2} \end{array} \right\} + \text{Al-Silicate (amorphous?) + SiO}_2 + \text{HCO}_3^- + \text{H}^+ \rightleftharpoons \left. \begin{array}{l} \text{K}^+ \\ \text{Mg}^{+2} \end{array} \right\} \text{Al-Silicate (amorphous or crystalline) + CO}_2 + \text{H}_2\text{O}$	Little	Little	None (?)
7. Same as 6 with initial crystalline Al-Silicate	Little	Little	None
8. Exchange reaction $\text{Me-Clay} + \text{Me}^{++} \rightleftharpoons \text{Me}_2\text{Clay} + \text{Me}^+$	Much	Much	None
9. $2\text{Mg}^{+2} + 3\text{H}_4\text{SiO}_4 + 4\text{OH}^- \rightleftharpoons \text{Mg}_2\text{Si}_3\text{O}_8 + 6\text{H}^+$	Some	Some	None
10. $\text{H}_4\text{SiO}_4 \rightleftharpoons \text{SiO}_2 + 2\text{H}_2\text{O}$	Much	Some	None
11. $\text{H}_4\text{SiO}_4 \rightleftharpoons \text{SiO}_2 \cdot n\text{H}_2\text{O} + (\text{H}_2\text{O})$	Some	Some	Much
12. Reactions with basalts on the sea floor	Little	Little	None

only 10^{13} moles of calcium are delivered to the ocean each year by rivers. Thus, more than 90% of the carbonate precipitated each year must redissolve if the ocean is to maintain a constant composition (Chave and Smith, 1972). It is not at all clear where this resolution occurs.

Reaction 2. Seawater is about one-fifth saturated with respect to gypsum. Thus, for this reaction effectively to remove SO_4^{-2} from seawater, significant evaporation must occur. There appear to be too few marginal hypersaline seas in the modern oceans to affect significantly the SO_4^{-2} concentration in the ocean. Perhaps in the past this mechanism was more effective.

Reactions 3 and 4. Anoxic conditions are necessary for the reduction of sulfate to sulfide and for the precipitation of metal sulfides. Although Berner (1971) presents some thermodynamic data on the metastable ferrous sulfides, there is still much to be learned. Precipitation of hydrous

sulfides is known to occur in the Black Sea, estuaries, fjords, and other restricted environments, but these areas are probably too small to affect the SO_4^{2-} concentration of seawater. Because of the restricted areas in which Reactions 2-4 can occur in the ocean, it is likely that SO_4^{2-} is increasing in concentration in seawater.

Reaction 5. A higher degree of evaporation is required to precipitate halite than gypsum. Thus, the question asked under Reaction 2 is even more significant. In that no other mechanism for chemical removal of sodium and chloride is known (except possibly Reaction 12), we must conclude that these elements are increasing in concentration in seawater.

Reactions 6 and 7. Reactions of some aluminum silicates have the potential of removing SiO_2 , HCO_3^- and cations from seawater or near-surface interstitial waters. Although aluminum silicates are present in all oceanic environments, there is little evidence that reactions are occurring. Because the exact nature of the aluminum silicates entering the sea from rivers is unknown, predictions of the kinetics or the location of these reactions are impossible.

Reaction 8. Exchange reactions of metals on clays have been thoroughly studied. They do not appear to be of sufficient magnitude to regulate the concentration of ions such as K^+ and Mg^{+2} in seawater.

Reaction 9. The precipitation of sepiolite should occur in seawater or in near-surface interstitial waters. There is little evidence that it does. The regulation of Mg^{+2} in seawater by any combination of Reactions 6-9 is still a puzzle (Drever, in press).

Reaction 10. Anhydrous silica (quartz, trydimite, or chrystobalite) does not appear to react with seawater although it is commonly undersaturated with respect to these phases. Some deep Pacific waters are supersaturated with respect to quartz, yet no reactions appear to be occurring there (Wollast, in press).

Reaction 11. Biogenic opal ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) is precipitated in enormous quantities in surface waters of the ocean as diatom and radiolarian tests. All seawater and near-surface interstitial water is undersaturated with this phase, and at most only a few percent of this opal reaches the sea floor. It is not known where or how this resolution occurs. Wollast (in press), and Hurd (1972a,b) have suggested some mechanisms.

Reaction 12. The hydration of basaltic glass on the sea floor and subsequent reaction of the hydration products with seawater may remove cations from seawater. Little is known about these reactions.

Many questions regarding mechanisms and locations for the regulation of major constituent concentrations in seawater are mentioned above. Although reactions that are probably valid can be written, the locations of these reactions in the ocean system are essentially unknown. A summary of our ignorance on these matters is given in Table 3.

TABLE 3
Location of Chemical Reactions in the Ocean

Element	Air-Sea Interface	Photic Zone	Continental Boundaries	Bulk Ocean	Deep/Seafloor
(SO_4^{2-})	Lost as aerosols, but rapidly returned to the ocean by rivers.	Precipitation very important. Solution unknown.	Precipitation important. Solution in low pH environments locally.	Precipitation unimportant. Solution may be important.	Precipitation unimportant. Solution may be important.
	As above	No reactions	Only possible sink for oxidized sulfur. Importance probably small.	No reactions	No reactions
(S^{2-})	No reaction	Possibly important due to photo-synthetic sulfur bacteria.	Only probably sink for reduced sulfur. Importance probably small.	No reaction	Possible sink in interstitial waters. Importance unknown.
	Lost as aerosols, but rapidly returned to the ocean by rivers.	No reactions	Only possible sink for Cl. Importance probably small.	No reaction	No reaction
	As above	No reaction	Only significant sink for Na. Importance probably small.	No reaction	Possible uptake by hydrated basalt. Importance unknown.
	As above	Possible reactions with Al-silicates. Importance unknown.	Possible reactions with Al-silicates. Some precipitation as Mg-calcites. Importance unknown.	Possible reactions with Al-silicates. Importance unknown.	Possible reactions with Al-silicates. Importance unknown.
	As above	As above	Possible reactions with Al-silicates. Importance unknown.	As above	As above
	As above	As above	As above	As above	As above
HCO_3^-	Nearly all HCO_3^- must return to the atmosphere as CO_2 through this interface.	Involved in all carbonate and Al-silicate reactions. Importance unknown.	As with photic zone	As with photic zone	As with photic zone
SiO_2	Unimportant	Biogenic precipitation very significant. Resolution may be significant because of higher temperature and pH, and low Si. Important. Importance of Al-silicate reactions unknown.	Al-silicate reactions may be important.	Solution of biogenic opal slower than photic zone because of lower temperatures and pH, and higher Si. Importance unknown. Al-silicate reactions probably not important.	Small percentage of biogenic opal reaches the sea floor. Al-silicate reactions unknown.

Although Table 3 can be basically summarized as "significance unknown," two locations for many of the reactions are suggested which have been little studied from the point of view of controlling mechanisms of major seawater constituents. These are the continental margins and the photic zone. We should (1) carefully investigate these areas using new field techniques such as in-situ sensors, (2) characterize the highly reactive, amorphous phases, and design experiments to study their thermodynamics and kinetics, and (3) consider and experiment in the field and the laboratory on the possible effects of organisms on major constituents, as well as conventional nutrients and organic phases.

The Physical and Chemical Properties of Seawater

The bulk thermodynamic and transport properties of seawater (such as P-V-T data, viscosity, conductivity, specific heat, enthalpy, freezing point, sound absorption, etc.) are useful to describe physical oceanographic processes such as adiabatic mixing and deep sea stability. Although numerous measurements (Pytkowicz and Kester, 1971; Millero, 1973a,b) have been made on the physical properties of seawater, there still is a need to reconcile the differences that exist between various investigators. For example the P-V-T properties (the equation of state) and the sound absorption of seawater need further work. There is a need for a reliable equation of state for seawater for deep-sea stability calculations. One method of deriving a reliable equation of state for seawater is to calculate compressibilities from sound velocity and specific heat measurements by an iterative technique (Crease, 1962). Since one can measure sound velocities with great precision, and the difference between adiabatic and isothermal compressibilities is small, the compressibilities derived from sound velocities are more precise than those determined by direct methods (Fine, Wang and Millero, 1973). Unfortunately, the velocity of sound measurements made by Wilson (1960) and Del Grosso and Mader (1972) are not in good agreement at high pressures and low temperatures (the oceanographic range of importance for deep-sea stability calculations). These discrepancies must be reconciled before we can derive a reliable equation of state. Direct measurements on the P-V-T properties of seawater with accuracies approaching those of sound velocity measurements (Millero, Knox, and Emmet, 1972; Emmet and Millero, 1973) would also yield useful data. It is important that all the P-V-T properties (as well as the other physical-chemical properties) of seawater be directly related to pure water. The reason is twofold: first, pure water is the working standard for the P-V-T properties of liquids, and if corrections are needed in the future they can be made; second, and probably more important, by examining

the difference between the P-V-T properties of seawater and pure water, one can magnify the effect of sea salts, which is what one is normally interested in when studying the oceans.

The most useful form of an equation of state would be one formulated in terms of the contributions of each significant solute. This would make the equation of state applicable in regions where special conditions prevail, such as in the Red Sea, or in low salinity regions near rivers or ice. Such an equation would reduce to that of pure water for zero salinity, and would account for the contribution of each significant solute.

Recent work on sound absorption in the ocean has opened up several questions concerning pressure-dependent chemical equilibria and chemical relaxation processes in the ocean. It is clear that the Schulkin and March equation (1962), originally developed to account for sound absorption due to the relaxation of magnesium sulfate in the ocean cannot explain the following anomalies:

- The low-frequency relaxation of 1 kHz deduced by Thorp (1965) from his analysis of long-range, deep sound channel acoustic propagation. The absorption below 1 kHz is greater by a factor of ten than predicted.

- The decrease with pressure of sound absorption in the 30-150 kHz region observed by Bezdek (1972, 1973). The pressure effect is greater by a factor of two than predicted.

- The asymmetry in absorption-per-wave-length plots in real seawater in the 30-300 kHz region obtained recently by Bezdek (1973) in the ocean and also in the original work by Wilson (1951) in the laboratory. This implies another relaxation between 1 kHz and the MgSO_4 absorption at 60 kHz.

The kinetics and equilibria responsible for these effects need to be identified by careful laboratory measurements of sound absorption from 500 Hz to 300 kHz due to the various solutes in seawater whose concentrations are above 1 ppm. The synthetic seawater used by early investigators omitted boric acid which, according to temperature jump work by Fisher, Yeager, Miceli, and Brussel (1972), could be the cause of the 1-kHz relaxation. The asymmetry in the high-frequency plot may be due to magnesium bicarbonate which Garland and Atkinson (1973) predict, on a theoretical basis, to have a relaxation frequency in the 10-kHz region.

Chemical Interactions Among the Major Components

Knowledge of ionic interactions in multicomponent electrolyte solutions like seawater and body fluids is necessary (Millero, 1971a, 1973a)

for an understanding of the physical and chemical properties of the medium. These interactions also are important because they affect many of the chemical processes that occur in seawater. For example, short-range interactions in seawater have been shown to affect the pH of the oceans (Weyl, 1961), the solubility of minerals in the oceans (Garrels, Thompson, and Siever, 1961), and the ultrasonic absorption of the oceans (Liebermann, 1949; Fisher, 1967).

Classically the ionic interactions in seawater have been treated by using Bjerrum's (1926), ion-pairing model as exemplified by the work of Garrels and Thompson (1962), Kester and Pytkowicz (1968, 1969, 1970), Atkinson, Dayhoff, and Ebdon, 1972 and Hawley, 1973. This approach formulates the electrostatic cation-anion interactions in terms of equilibrium constants that can be determined at the temperatures, pressures (Lafon, 1969; Kester and Pytkowicz, 1970; Millero, 1971b; Millero and Berner, 1972), and chemical environments characteristic of the oceans (Kester and Pytkowicz, 1968, 1969, 1970). The results of these methods have been successful in accounting for the activity coefficients of many solutes in the seawater medium (Kester and Pytkowicz, 1968, 1969, 1970), for the solubility of some minerals in the ocean (Garrels, Thompson, and Siever, 1961), and for the ultrasonic absorption of seawater (Fisher, 1967). Recently, the ion-pairing model has also been useful in explaining the Raman spectra of multicomponent sulfate solutions (Daly et al., 1972). An alternative approach that has been developed recently (Millero, 1971a, 1973a,b) considers ionic interactions in more general and less mechanistic terms. The model simply states that any physical property of seawater (P_{SW}) is equal to the property for pure water (P_{H_2O}) plus a contribution from the weighted ion-water interactions of the major components and one from the weighted ion-ion interactions of the major components:

$$P_{SW} = P_{H_2O} + \text{ion-water interactions} + \text{ion-ion interactions.} \quad (1)$$

The first two terms can be estimated from infinite dilution data in single-salt solutions (binary mixtures of salt + H_2O). The third term can be divided into a theoretical Debye-Hückel Limiting Law term and a term arising from deviations from the Limiting Law of the weighted major ionic components. This general approach of examining the physical-chemical properties of seawater serves two purposes. First, it provides the theoretical concentration dependence of the physical-chemical properties and second, it emphasizes the importance of ion-water and ion-ion interactions of major components of seawater.

Preliminary applications of these methods to the thermodynamic and transport properties of seawater have been successful (Millero et al., 1973, and Millero, 1973a,b). All of this preliminary work has been

carried out using data for single-electrolyte solutions. Further refinements must await more reliable single-electrolyte data as well as data for the excess thermodynamic and transport functions.

Measurement and Prediction of the Properties of Solutes in Seawater

One of the most important problems in examining chemical reactions in seawater is the estimation or prediction of the thermodynamic and kinetic properties of solutes (ionic and non-ionic). The thermodynamic equilibrium of a chemical process $A + B \rightarrow C$ can be characterized by an equilibrium constant

$$K = \frac{a_C}{a_A a_B} = \frac{[C]}{[A][B]} \cdot \frac{\gamma_C}{\gamma_A \gamma_B}, \quad (2)$$

where a_i , $[i]$ and γ_i are the activity, concentration, and activity coefficients of species i . The effect of pressure on K is given by

$$\left(\frac{\partial \ln K}{\partial P} \right)_T = - \frac{\Delta \bar{V}}{RT}, \quad (3)$$

where

$$\Delta \bar{V} = \bar{V}(C) - \bar{V}(A) - \bar{V}(B). \quad (4)$$

$\bar{V}(i)$ is the partial molal volume of species i .

The effect of temperature on K is given by

$$\left(\frac{\partial \ln K}{\partial T} \right)_P = \frac{\Delta \bar{H}}{RT^2},$$

where

$$\Delta \bar{H} = \bar{H}(C) - \bar{H}(A) - \bar{H}(B). \quad (6)$$

$\bar{H}(i)$ is the partial molal enthalpy of species i .

The determination of the equilibrium constant, its pressure dependence (Millero, 1971b; and Millero and Berner, 1972), and its temperature dependence can be made by (1) direct measurements in seawater (Kester and Pytkowicz, 1968, 1969, 1970), and (2) estimation from known properties of pure water and simple solutions (Millero, 1971a,b). To provide information in the absence of direct measurements, it is important to develop methods to estimate the activity coefficients, the partial molal volumes, and partial molal enthalpies of solutes in seawater.

Direct measurements of some selected systems (e.g., the ion complexing of metal ions) must also be made because they serve as a check for the various estimates. Several methods have been developed to predict activity coefficients, partial molal volumes, and enthalpies of solutes in seawater. Some of these are semiempirical (based on direct measurements in seawater), while others are theoretical (based on measurements in pure water). Further work is needed to determine which method is more useful. Since there are considerable thermodynamic and kinetic data available in pure water, estimates based on pure-water data could prove to be the easiest and fastest to make.

MINOR ELEMENTS

Chemical processes involving minor constituents in the ocean may be either homogeneous (within the solution phase) or heterogeneous reactions (at a solution-solid phase or solution-gas interface). Knowledge of the homogeneous reactions, such as chemical complexation and redox transformation, is important in assessing and predicting the chemical reactivity of minor elements in seawater. Understanding heterogeneous reactions, such as adsorption, ion exchange, precipitation, and dissolution, is necessary for considering the flux of materials through the ocean. Evaluations of these fluxes were considered in detail in Session C; the concern here is to identify the processes and to indicate those that should be emphasized in future research.

A characterization of chemical reactions implies the quantification of both their equilibrium and kinetic aspects. However, to apply this information in the marine environment, we must identify the sites at which active chemical processes occur. Analytical studies and *in-situ* experimentation in the ocean will reveal the locations of active chemical processes.

Knowledge of inorganic chemical processes involving minor constituents is important for a variety of reasons. For one, these reactions determine the nonbiological cycling of trace elements in the marine environment. The impact of man's activities on the ocean is largely determined by the fate of chemical substances added to the sea. Conversely, the effect of the environment on man's activity within the ocean depends on some of these processes. Minor elements can serve as sensitive indicators of biochemical and geochemical processes in seawater and sediments, and some of these constituents may be related to biological productivity. Some of the reactions involving minor components are significant in the formation of economically important substances such as ferro-manganese and phosphate deposits.

Homogeneous Reactions

A complete understanding of the distribution of trace elements in the oceans requires a knowledge of the forms—free and combined—in which these elements occur in seawater. The speciation of trace elements in seawater is poorly known, and trace elements are often characterized as either “soluble” or “particulate.”

Present knowledge of trace-element speciation is based on a variety of experimental techniques. The distribution of trace metals between free and complexed forms has been calculated from thermodynamic data (Goldberg, 1965; Stumm and Morgan, 1970). These calculations serve to identify the most important complexes, but their accuracy is often poor because of lack of knowledge of the activity coefficients of individual ions in seawater, and because of errors in the thermodynamic association constants themselves. Polarographic techniques such as anodic stripping voltammetry have shown that only small fractions of zinc, cadmium, copper, and lead are present as free ions at the normal pH of seawater (Zirino, et al., 1972; Zirino and Healy, 1972). This suggests that these metals are complexed with pH-dependent species such as bicarbonate, carbonate, and hydroxide. Separation techniques such as solvent extraction (Slowey and Hood, 1971) have shown that trace metals in seawater exist in both free and complexed forms. Association constants for iron-hydroxide complexes in seawater have been determined by potentiometric methods (Kester and Byrne, 1972).

Solving problems such as the behavior of radioactive tracers in seawater requires a better knowledge of the chemical speciation of these tracers. The use of radioactive tracers usually requires the assumption that the radioactive and stable isotopes of the tracer behave similarly. However, it is known that artificially produced zinc-65 does not behave in the same manner as does the naturally occurring zinc in seawater (Piro, Bernhard, and Verzi, 1972). This difference in behavior is because artificially introduced zinc-65 occurs in different forms than natural zinc. Similar differences in behavior may occur with other isotopes. This consideration is important in undertaking research involving radioactive isotopes such as that discussed in Session C and for tracer equilibration in analysis.

The speciation of trace elements in the sea must be studied using both field and laboratory techniques. Laboratory studies of the association of trace elements with naturally occurring inorganic and organic ligands in seawater will yield a knowledge of equilibrium speciation. Naturally occurring trace elements may be present in compounds that

are not in equilibrium with the seawater medium in which they are dissolved. For this reason, it is important that the chemical forms of naturally occurring trace elements be identified and their concentrations measured.

Laboratory studies and model calculations of trace-element associations should include the major inorganic ligands in seawater: chloride, sulfate, bicarbonate, carbonate, hydroxide, fluoride, and borate. The measurement of association between trace elements and organic compounds is important, but these studies require a knowledge of the most important naturally occurring organic ligands, which is not available at present.

The kinetics and mechanisms of the reactions of trace metals with both inorganic and organic ligands is important for a complete understanding of trace-element chemistry. Some knowledge is available on the inorganic systems, but it must be extended to include the effects of the seawater medium, temperature, and pressure. The study of the organic systems must await a more detailed knowledge of important potential ligands in the organic composition of seawater (see pp. 61-62).

Laboratory studies of trace element speciation should be made in solutions that approximate the composition of seawater as closely as possible and must include the effects of temperature, pressure, redox potential, and hydrogen ion concentration.

Heterogeneous Reactions

Several types of heterogeneous reactions can be identified as being significant in the marine environment. The adsorption of substances such as dissolved metals and phosphate on suspended matter is believed to be important in the removal of some minor elements from seawater. Ion exchanges with adsorbed materials as it is subjected to compositional gradients in coastal and estuarine regions, or to pH gradients within the ocean, may produce variations in the concentrations of the minor constituents. The precipitation and dissolution of solid phases in seawater alter the distribution and sedimentation of some of the minor elements. The formation and entrapment of gas bubbles not only produce variations in dissolved gas concentrations, but also alter the acoustical properties of the environment, and may provide sites for chemical reactions that would not otherwise occur.

Adsorption—Existing knowledge of adsorption reactions in seawater has been acquired by observing the removal of specific minor elements such as zinc and phosphate from a solution by a particulate solid phase such as a clay mineral or natural sediment. This process depends on

several variables; the chemical form of the element in solution, the characteristics of the solid phase, and competing reactions for the adsorption sites. An adsorption process may be distinguished as a nonspecific physical type or as a stronger chemical interaction termed chemisorption. The type of process will determine the subsequent mobility of the minor element and the significance of competing reactions.

Adsorption as a chemical process in the marine environment has not received the intensive and definitive investigation it merits. Even though it is widely acknowledged as a significant process, we do not know its quantitative role in geochemical cycles nor the specific locations in the marine environment where it is most important. Studies in regions where rivers mix with seawater indicate that the greatest chemical transformations occur at salinities of several parts per thousand rather than gradually throughout the mixing range of salinities. Further knowledge of this process is important to evaluate the fate of both pollutants and natural injections brought to the ocean by rivers.

Several approaches can be suggested as possible ways to gain more information on adsorption reactions. Basic knowledge can be obtained through laboratory investigations of specific minor elements and specific solid phases. Consideration should be given to the effects of the medium on adsorption processes by duplicating as closely as possible the main constituents of natural waters. For example, the presence of carbonate ions may be important in the adsorption of those trace metals that form carbonate complexes. The use of added minor element tracers is hampered by the potential problems arising from the presence of nonequilibrium forms of the element in natural systems. Variables in the solution phase that should be considered for coastal adsorption reactions are temperature, pH, ionic composition, and the potentially synergistic effects of adsorbable minor constituents. The solid phase should be characterized in terms of its surface area, availability, and strength of adsorption sites. Laboratory investigations of this type for selected systems such as geochemically active metals (e.g., Al, Mn, Fe, Cu, Zn), toxic technological metals (e.g., Cd, Hg, Pb), radioactive elements (e.g., Cr, Co, Sr, Cs, Ra, Th, and especially Pu), and biologically important constituents (e.g., P, As, Se, Mo, I) will provide the information required to assess some aspects of their behavior at continental boundaries of the ocean. These assessments would be substantiated or refined by observations in the marine environment.

In addition to the factors affecting adsorption processes in coastal environments, the effects of pressure on the exchange of minor constituents in the deep sea should be considered. This effect may be significant for adsorption reactions on biogenic particles or within a nepheloid layer. The study of adsorption processes should recognize not only the equilibrium distribution of the minor element between the

solution and solid phases, but also the time scale or kinetics by which the exchange occurs.

In this consideration, an ion exchange has been identified as a process separate from adsorption; however, in practice these two are closely related, and the considerations of adsorption apply to a large extent to ion-exchange processes.

Precipitation and dissolution—The distribution of trace elements is affected by their incorporation into solid phases such as calcium carbonate (Thompson and Bowen, 1969), opal (Chester, 1965), and various metal hydroxides (Cronan and Tooms, 1969). The movement of these solids through the oceans and their alteration, deposition, and/or solution provide mechanisms for the transport of trace elements.

The incorporation of trace elements into calcium carbonate and opal is probably biologically controlled, and the transport of trace elements in these solid phases can be studied through analytical determinations of their concentrations in calcareous and siliceous tests, coupled with a knowledge of the rates of precipitation and solution of calcium carbonate and opal in the ocean. Our knowledge of trace-element concentrations in calcareous and siliceous tests and of the rates of solution of these tests is negligible. For instance, the chemical and biological factors influencing the oceanic distribution of barium must be known in studies involving the radioactive tracer radium-226, but the concentration of barium in calcareous and siliceous tests is not well known.

The properties, rates of reactions, and distribution of metal hydroxides, such as iron and aluminum, in seawater and in interstitial waters, are poorly known. These compounds deserve further study because of their importance in the formation of ferro-manganese nodules (Mero, 1965) and in the alteration of clays (Sillén, 1961).

Gas bubbles—Gas bubbles in the ocean have been considered in connection with their effect on the injection of air into seawater (Bieri, 1971; Craig and Weiss, 1971) and on gas exchange (Kanwisher, 1963; Atkinson, 1972). In shallow water, gas bubbles may be produced by biological processes such as oxygen production from photosynthesis and hydrogen sulfide and methane generation from anaerobic decomposition of organic matter. Extension of these studies, which have been carried out largely through analyses of noble gas saturation anomalies, will most likely continue to reveal unique information on the role of gas bubbles in the ocean.

It is generally assumed that bubble formation by *in situ* production is inhibited by hydrostatic pressure; however, it is still necessary to consider conditions that can stabilize small gas bubbles under relatively

high hydrostatic pressures. These might include interfacial tension of small bubbles on solid surfaces, or surface active films under high compression at the bubble-solution interface.

Progress has been made in characterizing the size distribution of bubble populations in the surface layers of the ocean (Medwin, 1970). This effort should continue to be pursued, along with chemical characterization of the bubbles. Classical studies of the stability and dissolution of bubbles in seawater (Wyman et al., 1952; Liebermann, 1957) should be extended, where possible, to smaller bubbles and to include consideration of their behavior in the presence of surface active substances and solid surfaces.

Air-Sea Interface

In recent years there has been intensive consideration of chemical processes that occur at the air-sea interface. Some of these processes can be related to bubbles and the mechanisms by which they burst through the interface, producing chemical fractionation in the droplets injected into the atmosphere (Bloch and Luecke, 1972; and MacIntyre, 1972). However, there also appear to be other unique chemical characteristics of the air-sea interface that affect the minor elements of seawater. Duce et al. (1972) demonstrated the near-surface enrichment of such components as iron, lead, copper, and fatty acids. The specific processes involved in this enrichment have not been clearly established, although it is assumed that minor element association with surface active organic material is a significant factor. These mechanisms should be determined and the chemical stability of surface active materials on the sea surface must be examined. Factors to be considered are the breakdown of surface active materials by wave action, or chemically, photochemically, or by biochemical oxidation.

Examination of near-surface gradients of phosphate (Goering and Wallen, 1967) and of others that undoubtedly occur for other minor constituents may provide significant clues about the processes occurring near the air-sea interface.

Analytical Studies

Historically, the direction of effort to investigate an important chemical process has been dependent to a great extent on the availability of a useful analytical method. The solution of analytical problems continues to be of crucial importance (Carpenter, 1972) in the study of trace-element chemistry of the marine environment. It is necessary to have

techniques available not only to study the distribution of total concentrations of trace elements in seawater but also to distinguish between weakly associated and complexed forms or other important physico-chemical states (i.e., speciation).

Although the appearance of a powerful new technique may permit the investigation of a minor element not previously considered, a major effort should continue to be undertaken in the refinement of techniques presently being applied to the study of any of the minor elements. These efforts help locate active sites of chemical processes in the ocean environment.

At the present time, it is difficult to decide when variations in measured metal concentrations among various investigators are real differences or artifacts caused by different, arbitrarily chosen, sampling and pretreatment methods. A serious effort to continue to develop techniques for the construction and operation of noncontaminating sampling devices is needed. Existing commercial and laboratory-built samplers should be checked for adsorption and exchange reactions involving the minor element to be determined from the sample.

The problems of sample storage and shipment also remain unsolved. Most investigators have arbitrarily chosen a certain container material and subject the sample to some treatment such as acidification, freezing, freeze-drying or the addition of preservatives such as mercuric chloride. This has been operationally necessary to obtain any data at all, but the consequences of such treatment on any given minor element are not necessarily known. Also, existing methods for determining minor elements all suffer to some extent from the lack of intercalibration and standardization. The results of the Geochemical Ocean Sections (GEOSECS) intercalibration attempts (Brewer and Spencer, 1970) show that a perfectly reasonable and timely project in chemical oceanography is the calibration of methods. The question of how to store and ship standards is unsolved. Research should be undertaken on the development of sets of solids, soluble powders, standard solutions, and seawater samples with sufficient integrity to permit intercalibration for perhaps several years.

Our ability to make direct measurements of trace-element concentrations in the oceanic environment is in many cases inadequate. A concerted effort should be made to refine and extend the use of presently available methods such as atomic absorption, polarography, and specific-ion electrodes. At the same time, strenuous efforts should be made to apply other spectroscopic techniques such as UV-visible spectroscopy to direct and *in situ* measurements.

The valuable information from the *in situ* equilibrium measurements of Ben-Yaakov and Kaplan (1971), Petersen (1966), and Berger (1967)

point up the need for more measurements of this type. More equilibrium methods—both heterogeneous and homogeneous—should be developed and applied, and the development of *in situ* kinetic methods should be explored.

One of the great unknowns in trace-metal speciation studies is the role of organic ligands. The characterization of classes of compounds and individual organic species is a well-developed field of chemistry. However, the enormous variety and overall low concentration of organic species in the ocean make *in-situ* measurements improbable. Previous comments on sampling and standardization obviously apply here. Once these steps are taken, the enormously powerful battery of new techniques used by organic and biochemists can be applied—Fourier Transform infrared and nuclear magnetic resonance spectroscopy, computer-assisted gas chromatography, mass spectrometry, gel permeation, and high-pressure liquid chromatography.

Finally, chemical oceanographers must be encouraged to adopt and adapt the highly developed analytical methods used in other areas of science. Examples are the sensitive analytical methods developed for lunar rock analysis and the recent advances in clinical analytical chemistry.

THE ROLE OF ESTUARIES IN MODIFYING SEAWATER COMPOSITION

Streams bring a burden of dissolved and particulate substances to the sea, and in the region of encounter between fresh water and seawater a variety of processes occur to alter locally the composition of seawater. The natural phenomena occurring in this region provide the context for understanding the effect of man-induced changes in the quality and quantity of materials supplied to the estuarine zone. The coastal zone, therefore, provides an environment for modifying the composition of seawater that may be as important as the open-ocean environment. Some fundamental problems in this area are

1. The flux of dissolved elements to the ocean from streams is known fairly well on a worldwide average basis for the major components. However, seasonal changes in the chemical composition of streams as they enter the ocean are not well understood, and a few reliable data on trace constituents are available.

2. The quality and quantity of sediment loads brought to estuarine environments by rivers require attention. For example, the total quantity of sediment delivered by the Susquehanna River as the result of hurricane Agnes in 1972 equaled the total sediment load transported in the past 50 to 100 years. This large supply of fresh water and sediment seriously

altered both the chemical properties of the estuarine water and the physical and chemical properties of the sediment in Chesapeake Bay. Similar areas of interest occur throughout the United States and the world, each with their own erosional and hydrological characteristics.

3. A major study of the dissolved and particulate trace-element burden of streams is required. There is good evidence that organic particles, especially, act as a major carrier of trace metals to the sea where subsequent estuarine processes may release the metals to seawater. On the basis of sediment and water studies it is clear that as much as 80% of the content of some trace elements and organic particles are released to the estuarine water. The release mechanism is not known. It may in part be released by ion exchange, in part by biological degradation of the organic carrier of the metals, processes that also occur in the open ocean.

4. The fate of metals and silica in estuarine waters must be assessed to understand not only the pathway of these elements brought to the estuary by streams, but also the modifying role of open-ocean seawater when it encounters the coastal zone. We know that in areas where the supply of organic matter from the continent is great and biological productivity in the adjacent marine environment is high, organic matter accumulates rapidly in the sediment, and sulfate reduction occurs. Silica is deposited rapidly by diatom productivity in the same areas. The high sulfide-ion concentration results in the sequestering, as sulfide, of many trace metals released in the sediment from *in-situ* organic degradation. The result of this process is to extract many metals from seawater, reducing their concentrations in open seawater. This is especially true for mercury, lead, gold, and silver. Iron and manganese (and possibly other metals) may be exceptions to this because of the higher solubilities of the sulfides of the doubly charged ions of these two elements. Hence, a flux of iron and manganese out of an estuary is possible. These processes are now mainly understood intuitively on the basis of the composition of sediments and thermodynamic arguments. Experimental and direct observational confirmations are required.

One aspect of trace-element studies in estuaries, including both radioactive and stable nuclides, involves the transfer of minor elements from polluted rivers and estuaries to the sediments. One can observe the disappearance of lead, cadmium, and similar metals from the water column near shore at a rate faster than can be accounted for by dilution. Analysis of sediment cores reveals that the sediments are a sink for these pollutants. However, the processes of transfer are difficult to define. The chemical forms of the accumulated metals in the sediments may not be related to those in the water column because of the rapid transport and mixing of the sedimentary material. The sampling problem

is serious but might be resolved in shallow water areas through the use of research submersibles. Near-bottom sensors and samplers might be set in place and the accumulation of sedimentary material be observed without washing out or exchanging with nearby sediments. If truly representative samples could be obtained, and if the rate of sedimentation could be inferred from the collected material, the pathways of the pollutants might be elucidated.

PARTICULATE MATTER

A first-order feature of the density field in the ocean is the shallow pycnocline. This boundary coincides approximately with the bottom of the photic zone and forms a barrier to mixing between the upper few hundred meters and the deep sea. The water above the boundary is the immediate recipient of all the continentally derived dissolved and particulate material. Particles introduced or formed in this layer can sink through the mixing barrier (a one-way process) into the deep water, thereby depleting the surface water of their constituents.

At the present time the particulate flux in the ocean is similar in many respects to the “ether” of 19th century physics in that its nature is more described by the effects attributed to it than by experimental observation. These observational data on dissolved trace constituents are explained in terms of scavenging.

One of the central problems of marine geochemistry is to resolve by *direct measurement* the source and composition of the particles constituting the nepheloid layers as functions of space and time. The main study areas can be categorized as follows:

- Physics — Size frequency distribution
 - Density contrast with water
 - Settling rates (Stokesian or not)
 - Effect of turbulence and shear.

These factors determine the vertical flux of material and its concentration in the water column and how much water has to be collected to obtain a statistically significant sample. It is necessary to calculate reasonable sedimentation rates from measured fluxes to determine the available surface area for reaction and the transit time through the water column.

- Chemistry — Identification of organic and inorganic phases and their temporal and spatial variations
 - Radioisotope analyses to determine injection and settling rates directly (Pb-210, Fe-55, Si-32, C-14, Ra-226, Pu-238 and 239)

- Scavenging and dissolution processes (require parallel measurements in the water column and accounting for lateral motions that may amount to thousands of miles).

These studies would give source functions for the *in situ* production and consumption of dissolved materials. They are particularly important for the radioactive constituents, especially the plutonium isotopes discussed in Session C. They would also indicate to what extent the various species dissolve on the bottom or during sinking.

Analyses of particulate matter collected from the water column should include

1. Physical composition and morphology by x-ray diffraction, scanning electron microscopy, electron probe, and biological species identification (size, frequency, and distribution)
2. Chemical: Elemental composition of the organic fraction; C:N:P ratios; characterization of protein, lipid, and carbohydrate components; composition of inorganic fraction by neutron activation, x-ray fluorescence, atomic absorption, mass spectrometry, and leaching experiments
3. Radiochemical analyses: Silicon-32, carbon-14, and radium-226 to be determined on all samples, Lead-210 and thorium isotopes on the upper portion of bottom samples and iron-55 and other artificially produced isotopes on shallow samples
4. Stable isotope measurements.

ROLE OF BOTTOM DEPOSITS IN MODIFYING SEAWATER COMPOSITION

In addition to the controls of clay and calcium carbonate on the overall chemical state of seawater, there are specific modifications in the concentration of trace and minor components in the water column resulting from processes occurring at the ocean bottom. None of these processes is as yet sufficiently understood, especially with regard to their relative importance in modifying the composition of seawater. The specific areas needing more research include

1. The flux of elements in and out of the water by reactions with igneous rocks on the ocean floor
2. Transport to the deep ocean of elements brought in by hot fluid transport from depth
3. The effect of minerals in sediments which sequester elements from seawater and interstitial waters. In particular, the flux of radium-226 and radon-220 to the deep ocean from bottom sediment will be controlled by the presence or absence of radium traps such as barite and phillipsite in the sediment. These two nuclides are of interest in ocean circulation

studies. Similar constraints can be anticipated for other elements. The mode of manganese and iron oxide deposition on the ocean floor and its role in modifying ocean chemistry are still not well known.

4. The movement of bottom sediments by bottom currents or down-slope movements may result in the solution of some components such as biogenic silica and calcium carbonate but may also transport them into deep pockets where they are protected from solution. The injection of silicon-32 with stable silicon into bottom water originating in the Antarctic region by the solution of biogenic silica during current transport is of interest in deciphering water paths and the material balance for both silicon-32 and stable silica. The association of barium with biogenic silica deposits in the Antarctic region is of importance in understanding the geochemical cycle of this element. Sedimentation rates in the deep sea should be measured using isotopes with different half-lives to estimate the flux of material into bottom waters.

5. The environment of the midocean ridge areas is different from that of the abyssal plains in a number of ways that can influence the composition of the sediments of this region. The association of high concentrations of calcium carbonate, barium, organic matter, and some metals with the high ridge areas has been described. The reasons for each of these elements being found in the same general location may not be the same. Biologic, sedimentologic, and volcanic causes may combine in one location to give the end result of enrichment of chemicals along the ridge area. To understand the environment of the ridge area, it is important to unravel these processes. The use of research submersibles is admirably suited to such studies of the ridge. Further consideration of fluxes at the sediment-sea interface are contained in pp. 62 to 84 of this document.

NUMERICAL MODELS IN CHEMICAL OCEANOGRAPHY

One major area that has been neglected in chemical oceanography is the incorporation of major and minor element distributions into ocean circulation models. An important ingredient of such models is an understanding of the chemical and physical processes that alter the concentrations of elements within the water column. A water mass is an open system that exchanges material by advective and diffusive processes, and interacts with the descending particulate flux. Simple mass balance models are often adequate for such concepts as apparent oxygen utilization (AOU). However, such concepts oversimplify the complex nature of the actual processes occurring in the oceans. The first aspect of the modeling process should emphasize the incorporation of transport and particulate interaction terms into the simple mass balance.

The second important aspect of model calculations is the "feedback" of the chemical distributions as a check on the physical models. Even the simplest chemical systems such as dissolved oxygen and nutrients are characterized by much more complicated and variable distributions than those observed for temperature, salinity, and density. Incorporation of such components into the simple physical transport models provides a more stringent constraint for the model itself.

A third important aspect of the application of chemical variations to physical models is the increasingly important use of natural and artificial radioisotopes for to incorporate real time into the circulation models. The major radioisotopes presently useful for general circulation models are carbon-14, radium-226, and potentially silicon-32. These provide time scales of the order of 8000 years, 2000 years and 700 years for mixing and circulation studies. Each is involved in chemical and particulate interaction processes in the sea. Both stable carbon and radiocarbon are supplied to the deep sea by the oxidation of organic material and the dissolution of calcium carbonate contained in the particulate flux. The actual application of the radiocarbon "clock" to mixing and circulation processes demands a most careful and detailed study of variations in total dissolved inorganic carbon, dissolved oxygen, alkalinity, and the stable carbon isotope carbon-13, together with the measurement of specific activity variations of radiocarbon in the sea. Similar considerations apply to radium-226, which is involved in the particulate interaction problem and is introduced into the sea by diffusion from bottom sediments, and to silicon-32, which is involved in the stable silicon cycle in the sea.

As important class of constituents for model studies is the group of "stable-conservative" tracers, which differ in their relationships to salinity throughout the sea but are not altered by *in-situ* chemical processes. These constituents, which include some dissolved gases, the stable isotopic water molecules HDO and H_2O^{18} , and certain trace elements, receive their initial variability at the sea surface through air-sea interaction processes. Some of these tracers, such as helium-3 and helium-4, are injected into the sea at the bottom and in certain specific areas such as the crests of ocean ridges. These provide especially valuable localized tracers for regional circulation and mixing studies in deep and bottom water.

At the present time, several types of analytical and numerical models of varying complexity have been applied to the distribution of chemical and isotopic species. One-dimensional diffusion and advection models with *in-situ* production and consumption terms have been used for the carbon-12, carbon-13, carbon-14, oxygen and nutrient systems in the Pacific with encouraging results. Simple vertical diffusion models with constant and variable diffusivities have been applied to Radon

222 and radium-228 in both the surface layers and the bottom water. These results are useful for studying the air-sea and bottom-sea interchange of material. Several trace elements, notably copper, scandium, antimony, and nickel, have been studied sufficiently to show that vertical models should be useful in understanding their chemistry in the sea.

A second type of model currently being used for chemical constituents is a two-dimensional, horizontal diffusion and advection model. These models are based on "Stommelian" geostrophy with vertical advection balancing the horizontal inflow of water from western boundary currents which feed the interior regions of the world oceans. Conceptually, they are a natural extension of the simple "box models" that have been used successfully to understand the general nature of the vertical distribution of radioisotopes.

Physical oceanographers are extending these simple models account for such effects as topography and nonlinear terms in the equations of motion. A similar approach can be made with nonconservative species. To approach a realistic model of the chemical and particulate interaction processes in the sea, efforts should be made to develop three-dimensional models for describing oceanic processes. More emphasis on this aspect of chemical oceanography is urgently required to guide the future development of the subject and to insure a continual interaction with the developments made in physical oceanography.

Measurements of constituents of global fallout in the upper layers of the Pacific during the past decade have suggested that distributions of certain species may be dominated by lateral advection and lateral mixing in certain large areas, notably in the North Pacific Ocean. Large fractions of passive materials such as radiocesium have remained in the upper 300 for more than 10 years after entering as fallout (Folsom et al., 1968; Folsom et al., 1970; Hodge et al., 1972). For a period as long as this, one must expect advections of thousands of miles and take into account geographic and seasonal variations of inputs before attempting interpretations of vertical profiles. The sampling required for a model of this scale needs specialized procedures and specialized analytical methods. Nevertheless, a knowledge of the behavior of a passive material such as cesium or tritium seems essential for any study of the progress and chemical behavior of many other chemical species in the upper ocean layers. The advective parameter simply cannot be ignored in the model; however, chemical procedures can be evoked to discover their magnitudes.

Session B

Chemical Fluxes Through the Marine Environment, Including Air-Sea and Sediment-Sea Exchanges

Dr. Edward D. Goldberg, Discussion Leader

INTRODUCTION

How much material is being added to the present-day ocean by each of the various sources, and how much is being removed to each of the various sinks? For which components are these addition and removal rates changed as functions of time? These questions serve as a basis for investigating fluxes in the marine environment relative to further understanding chemical oceanography.

We must know how uniform the composition of seawater has been over geologic time intervals to interpret earth history from a study of ancient marine sediments. We must know the fates of various natural constituents added to the marine environment to *predict* how the ocean will respond to materials introduced by man.

A simple calculation using the area of the earth's surface covered by the ocean and the average depth of the ocean gives the volume of the ocean. The volume of river water added to the ocean each year is more difficult to determine, but recent estimates are in reasonable agreement. It appears that present-day river inflow would equal the volume of the ocean in about 40,000 years. Hence, water cycles from ocean to atmosphere and back vary rapidly on a geologic time scale.

The total dissolved salt content of seawater can be easily and accurately determined and is found to average about 35,000 ppm. The average total dissolved salt content of river water is much more difficult to estimate and is deserving of additional study, but recent estimates cluster around 115 ppm. Assuming no losses from the ocean through sedimentation, and with seawater about 300 times saltier than average river water, 300 transfer cycles from the continents to the oceans would be required to produce seawater salinity. This would take $300 \times 40,000$ years = 12 million years, which is a short time, geologically.

This kind of calculation is less meaningful than one which could be made considering each constituent individually, because seawater is different from river water in the ratios of its various components. The calculation, nevertheless, illustrates the point that the total salt content of the sea can be added in a very short time. It thus raises such questions as, What regulates seawater composition? and, Have such regulatory mechanisms been constant over geologic time periods?

Careful study of ancient marine sediments, their pore waters and fossils contained in these sediments, give little indication of any changes in seawater composition. Thus, a considerable effort has gone into explanations of mechanisms for maintaining a constant composition in seawater. The best known of these are the equilibrium models first proposed by Sillén (1961), and expanded by Holland (1965), Siever (1968), Garrels and MacKenzie (1971), and others. All of these models are somewhat vague in detailing the exact reactions occurring in the ocean, and little evidence has been found to indicate that the suggested reactions are occurring. At the same time, the models have been criticized on theoretical grounds (e.g., Pytkowicz, 1972) and seem not to be consistent with the actual solid phases found at the sea floor. Further work is needed on the interaction of minerals with seawater, as determined from their solubilities and rates of solution and precipitation. The available literature on this topic, including the effects of pressure which are vital for our understanding of the deep oceans, has been summarized in part by Pytkowicz and Kester (1971).

Broecker (1971) has proposed a kinetic model for the chemical composition of seawater, but he gives few specific examples of either supply or removal mechanisms for the major constituents of seawater, concentrating rather on the biologically active elements carbon, nitrogen, phosphorus and silicon. If we are to extend this approach, we need better data on the rate of supply and removal of various constituents from seawater. As mentioned above, the rate of supply of the major components by river water is not as well known as we would like.

The rate of supply of minor constituents dissolved in river water is even more poorly known, and the rates of supply of both major and minor elements as particulate matter and their subsequent release to the water are almost completely unknown. In the same way, the amounts of materials added to the oceans from undersea volcanic exhalations, springs, weathering of solid volcanic material, and the like, can only be grossly estimated at the present time.

Our knowledge of how dissolved materials are removed from the sea is little better than that of how they are added. The factors involved have been commented on elsewhere in this document (e.g. see Session C), and it is sufficient to note here that well-defined removal mechanisms exist for bicarbonate and calcium but for none of the other major con-

stituents. Sulfate is thought to be removed following biochemical reduction to sulfide, but the quantitative importance of this mechanism has not been evaluated.

Sodium and chloride leave the ocean waters primarily dissolved in pore water of sediments, and potassium by uptake by clays, but the quantitative aspects remain to be worked out. Practically none of the details of how magnesium or any of the minor constituents are removed from the system is known.

PLUTONIUM CHEMISTRY OF THE OCEAN

Plutonium is an extremely toxic, radioactive man-made element whose behavior in the marine environment is inadequately known, although it has been studied intensively in connection with production of weapons and power sources (Olafson and Larson, 1963; Miner, 1964; and Coleman, 1965). Only a few determinations of its concentration in seawater and in associated organisms and sediments have been made, the first being as recent as 1964 (Pillai et al., 1964). Its chemical behavior in the marine environment will be difficult to predict from that observed on land, especially its involvement with the organisms of the sea.

Plutonium is a member of the actinide series and chemically similar to the rare earths. It forms insoluble fluorides and hydroxides, and a quite insoluble oxide. It can exist in several oxidation states, commonly as tri- and tetravalent cations, or in the hexavalent form PuO_2^{+2} . It forms soluble complexes with citrate and is strongly chelated (Olafson and Larson, 1963).

The use of plutonium is expected to expand so rapidly that several serious hazards and management problems can be foreseen. Two of its nuclides, Pu-239 and Pu-238, are employed as fuels. Accidents released both of these into the environment, and, considering the large scale of projected nuclear power programs, more such accidental releases can be expected. The transport of this valuable major fuel across oceans and continents may invite thievery and hijacking.

It is important to accelerate studies of background levels and to investigate chemical phenomena that might suggest the results of large additions of plutonium nuclides to the ocean. These studies should include consideration of its enrichment within the marine biosphere and its known affinities for inorganic surfaces and particles.

Present Conditions in the Ocean

The time of entry of most of the ocean's plutonium is fairly well known, as is its probable character on arrival at the sea surface. The largest fraction originated during 1950-1970 as global fallout which has

been documented by air and soil analyses (Hardy et al., 1972), or has been inferred from records of other bomb wastes.

Plutonium, similar to many metals, is enriched 1000-fold or more in many plants and animals. It appears to be retained for many years (Olafson and Larson, 1963; Miner, 1964) in larger terrestrial animals. Plutonium appears in the food of the larger marine animals; however, it has been found in much higher concentrations in members of the lower trophic levels. It has not been established which organs and tissues are involved in plutonium uptake by plankton. It may be that only surface adsorption is involved at these levels. Suggestions of this have come from findings of high plutonium concentrations on certain living and dead surfaces. The highest concentrations so far have been found in the outer 0.2mm layer of giant brown algae (Wong et al., 1972).

In seawater, the present plutonium-239 radioactivities are only roughly 2% of strontium-90 and cesium-137 radioactivities. The radioactivity of the shorter lived nuclide plutonium-238 is at present only 2 or 3% of the longer lived nuclide. Dialysis studies in Russia (Zlobin and Mokanu, 1970), suggest that plutonium may exist in seawater as colloidal particles (less than 0.1 to 0.3 microns), unless attached to larger particles.

Vertical distributions need to be known for chemical budgeting and other purposes, but the vertical distribution of plutonium is not well known. Sensitivity and precision are so low that many earlier measurements of deeper waters are suspect. However, there are several indirect measurements that suggest a loss from the upper layers that is more rapid than would occur with a completely passive material (one not associating itself with particulate materials, living or dead). Budgeting of concentrations in the Atlantic Ocean has yielded some scavenging rate estimates (Noshkin and Bowen, 1972). Likewise, some model-fitting of concentrations found by monitoring tissue concentrations in large oceanic fish in the Pacific Ocean has suggested a loss from the upper layers (where these fish live) of plutonium at the rate of half of that present in about 4 years, in contrast with about 10 years suggested for cesium (Folsom, 1972).

One outcome of recent plutonium studies has been the establishment of a large-scale turnover model for heavy metal nuclides in some special regions of the ocean. These studies suggest that one could follow minute changes for perhaps another decade in the upper layers of the Eastern Pacific Ocean. One now has some idea *where* to sample in order to detect a relatively small accidental increase of plutonium. The failure of SNAP-9A (in outer space in 1964) introduced about one kilogram of plutonium-238 into the ocean. This roughly tripled the amount already in the ocean (Hardy et al., 1972), and the addition can be measured with present methods.

Chemical and Radioactive Properties

Physical radiometric methods are now adequate for the two important alpha-emitting nuclides (Miyake and Sugimura, 1968), and although internal standards have been used in most cases, there is little indication that equilibration with the plutonium in seawater has been established. Plutonium's attraction to surfaces may be one of its most characteristic properties and needs additional study, beginning with the relatively simple surfaces of the large algae.

Describing oceanic distributions has been limited by low and variable analytical yields, especially in sediments and complex living tissues. Improved analytical methods are needed; one promising technique is the recovery of traces of plutonium from tissue by electroplating.

There are still other puzzles related to plutonium in the ocean. Why is it often associated with high concentrations of natural polonium on surfaces, and what brings them to these surfaces? Are the concentrating agencies physical, chemical, or biological? Do the nuclear properties (the alpha emissions) contribute anything to the processes? Has natural polonium-210 been significant in shaping the biosphere? Will the plutonium that may be added significantly increase the ionizing burdens?

FACTORS GOVERNING THE COMPOSITION OF SEAWATER BELOW THE POLAR ICE COVER

The intermittently ice-covered polar seas may be areas of strong air-sea gas exchange, as evidenced by the intense air-sea gradients observed there. These areas have been poorly investigated because of the sampling difficulties. The freezing process and the biota, unique to the ice-seawater system, many produce chemical conditions distinct from those of open sea regions.

The freezing of seawater and its effect on the chemistry of the water-ice interface is not well understood. There have been too few systematic field observations of the composition of surface seawater under freezing conditions to compare with data from laboratory investigations (Wiere, 1930; Thompson and Nelson, 1956; and Bennington, 1962).

Marine plants are abundant within and under the sea ice (Apollonio, 1961, 1965; Meguro et al., 1967; and Clasby et al., 1972), and their chemical interactions may differ noticeably from those of open ocean phytoplankton. It is important to determine the horizontal chemical gradients that may be produced under the ice and within the open water, and the rates of transfer of gases across the water-air interface in the open water. Adequate investigations of horizontal chemical gradients on scale lengths of a few meters to kilometers and of small-scale vertical gradients directly under the ice are difficult to carry out. The difficulty arises from

1. Hazards in working on an ice flow close to its edge
2. The inability to evaluate properly the physical, chemical and biological nature of the undersurface of the ice
3. The loss of sampling integrity caused by the borehole and contact of the seawater with the atmosphere
4. Serious disturbances that arise when making boundary-layer chemical observations from surface ships operating within the ice.

In regions that undergo surface freezing there are intense seasonal changes in dissolved carbon dioxide (Kelley, 1970) and probably in dissolved oxygen to a lesser extent. With the exception of major upwelling areas (Gordon et al., 1971; Kelley and Hood, 1971; and Kelley et al., 1971) and shallow coastal systems (Gordon, 1973), seasonal carbon dioxide variations in surface waters of the polar seas have shown the largest temporal variations in the world's oceans.

Many sampling problems might be overcome by using a research submersible that can maneuver under the ice as well as in the open water. This capability could be coupled with the use of *in situ* sensors (for salinity, temperature, pH, and dissolved oxygen), with control and visible observation of the sampling location, and with facilities for on-board data readout. Such capability would allow for the design of experiments addressed to the measurement of horizontal and vertical gradients under and at the margins of the ice and rates of formation and decay of these gradients. Information of this kind would provide valuable data bearing on the physical, chemical, and ecological processes acting in the polar seas.

PARTICULATE FLUXES IN THE OCEANS

The quantitative aspects of the transfer of particles from the upper layers of the ocean to its depths and the relative importance of each of the mechanisms of transfer are unresolved questions in chemical oceanography.

Vertical transport by settling particles is significant in governing the distributions of chemical species in the ocean. Such transport hastens the downward movement of radioactive contamination, pesticides, herbicides, or other products of man's activities. Our present knowledge of particles is largely confined to bulk compositional analyses, light-scattering properties, and theoretical settling rates. We need the ability to predict the properties of zones of high particulate load (i.e. nepheloid layers), the extent to which various substances in the sea will be incorporated in or upon settling particles, the rate of downward transport, and whether such material ultimately remains with the particle or escapes into the surrounding water.

Particles play a special role in the ocean. Such materials are introduced primarily by weathering processes and biological activities, but also by volcanism and chemical processes in the upper layers. Once formed, these materials settle, usually slowly, toward the seafloor and provide a site for various reactions. The bulk composition, size distribution and light-scattering properties have received considerable attention, particularly by Soviet investigators. However, we have only limited understanding of the changes that occur in and on particles after formation. Such particles play a key role in heavy metal transport, but the relative role of various particle types is not well understood, nor are we certain of the importance or rates of surface reactions on the particles.

Particles entering the sea and particles residing in the upper layers may be collected into aggregates with greater settling velocity and less areal exposure to seawater. Filter feeders ingest, grind, and digest particles, ultimately expelling them as fecal pellets, which settle far faster than the individual component particles. Moreover, the pellets are largely isolated from seawater by coatings, but they are fragile, often breaking soon after formation, and they may in turn be reingested, digested, and reformed. Nevertheless, a vast rain of such materials moves toward the seafloor. Their role in vertical transport depends on transfer across their boundaries, and their ability to remain intact under physical stress and bacterial attack.

Those pellets that reach the seafloor are broken or altered, with their contents subsequently being transformed by bacteria and ultimately released to the water and sediment. Most settling pellets are probably broken up by collection methods, and gentler collection techniques and more careful studies of the amounts, settling rates, and surface chemistry of such materials are needed.

Particles of continental detritus may settle rapidly in the coastal zone or slowly into the abyss. During settling these particles undergo varying degrees of equilibration with dissolved species in the water, exchanging ions, adsorbing, and even to some extent dissolving. Since the bulk of inorganic detritus enters at the ocean surface, rapid reactions will affect surface water chemistry, whereas slower reactions may have greater effect during the long slow fall into the depths. Our understanding of the rates of these reactions and their response to temperature and pressure is poor. The influence of squeezing temperatures, when different from the *in-situ* temperature, on the apparent composition of interstitial waters shows that many equilibria are markedly altered by temperature changes. Such factors influence the role of particles in redistributing chemicals in the sea, but we cannot assign quantitative values to this role.

The sinking of the tests of marine organisms plays a well-established role in the distribution of the nutrients in the ocean. A spectrum of trace

elements (e.g. barium, radium, and strontium) is carried along with the particulate silicates, carbonates, phosphates, nitrogen compounds and organic materials. Re-solution of sinking carbonates may affect the alkalinity, carbon and oxygen isotope ratios, and trace-element patterns. The kinetics of the dissolution and the true oceanic sinking rates need more study. Likewise, silicate tests are subject to dissolution as they sink, but there is little agreement on the balance between in-transit solution and bottom solution followed by upward mixing. The nature of this balance will affect the associated trace elements as well as the silicate distribution.

Casts of marine organisms discarded in the surface water during moulting may be rich in nutrients or trace metals. The rapid descent of such materials may constitute a significant transport mechanisms, but it also lacks quantitative evaluation.

Yet another problem is the fluxes of dissolved substances across the sediment-water interface. What are the magnitudes of these fluxes relative to other input or removal processes? Predictive models are needed to estimate the sink and source potentials of different sediment types for a given solute. It is also necessary to understand when a material that has settled to the seafloor is no longer chemically in contact with the ocean.

Models for solute flux across the sediment-seawater interface that balance supply and removal by dissolution/precipitation/relax reactions have been proposed (Crank, 1956; Shishkina, 1964; Berner, 1964,1971; Duursma, 1966; Anikouchine, 1967; Lerman, 1971; Tzur, 1971; and Hurd, 1972a,b). The apparent diffusion coefficient of a solute is a function of temperature, tortuosity, and any interaction the solute may have with the surface of the solid phase. These solid-solute interactions are being investigated (Duursma, 1970; Manheim, 1970; and Lerman, 1971), but the results have not been rigorously applied to real sediments. Present results, however, suggest that these corrections may reduce the value of the apparent diffusion coefficient of ions by as much as 3 to 5 orders of magnitude. If solids are dissolving or precipitating within the sediments, determinations of the heterogeneous solution rate constants must be made to compare laboratory data with models based on suspended matter and sediment. In the case of biogenic opal (Hurd, 1972a,b), dissolution rate constants of acid-cleaned radiolarians in seawater differed by 3 to 6 orders of magnitude from rate constants for sediments estimated by the models mentioned above. Other biogenic minerals such as calcium carbonate and apatite need to be similarly modeled because of the more rapid turnover through biogenic mineral formation than through inorganic precipitation of the same elements (Ca, C, O, Si, and P).

Sulfate reduction has been extensively studied (Berner, 1964) in recent sediments. It would be valuable to know the kinetics of particulate and dissolved organic carbon oxidation to complement such studies. Silicates are being modeled for equilibrium and kinetic considerations (Wollast, 1967; Helgeson, 1971; Luce et al., 1972), but the actual kinetics have been studied on few of these minerals. In every study using concentration gradients in sediments for modeling, the physical properties of sediments should be determined to allow at least first-order tortuosity corrections for the diffusion term using porosity measurements.

Estuarine and shelf sediments are less completely studied than deep-sea sediments. Because of the higher sedimentation rates, larger pH-Eh fluctuations, more active bioperturbation of sediments and their higher organic contents, their chemistries are more varied and invite additional study. The sediment-water interface must also be studied more closely to understand the transition from particulate suspended matter to actual sediment. Concentration profiles in the water above the sediment have only been measured by sampling devices that disturb the system sampled. While such devices provide useful information for large-scale gradients (e.g., 1 to 10 m), it may be possible to observe the actual interface gradients only by using *in-situ* devices over 1- to 3-month periods. Measurements of the radon flux should be attempted to estimate mixing and turbulence for the bottom waters.

DETERMINATION OF THE EXCHANGE OF GASES BETWEEN THE ATMOSPHERE AND THE SEA

Much remains to be learned about regional and mesoscale air-sea transport of gases. Predictive models related to man's modification of the atmosphere and ocean depend vitally on information of this sort.

Human activities have brought about changes in the balance of gases dissolved in the oceans and present in the atmosphere (Bolin and Eriksson, 1959; Broecker et al., 1971; and Machta, 1972). These changes range from the introduction of trace and bulk constituents, such as by-products of civilization, to the possible alteration of natural processes by agricultural and industrial activities (Goldberg, 1971). Since the International Geophysical Year, continuous clean-air baseline measurements of several atmospheric gases have led to the discovery of secular increases in their content in the atmosphere. These increases have been most evident in the case of carbon dioxide (Brown and Keeling, 1965; Pales and Keeling, 1965) and more recently in tropospheric ozone (Komhyr et al., 1971; and Kelley, 1972).

For carbon dioxide, it is estimated that 30 to 40% of the input by man to the atmosphere has entered the sea (Machta, 1972; Broecker et al.,

1971). Regional rates of exchange, however, have been estimated only from a few calculations, based on local carbon dioxide partial pressure and wind data (Teal and Kanwisher, 1966), from changes inferred in surface-water oxygen content resulting from biological processes, based upon consideration of changes in nutrient distributions (Redfield, 1948), from recent indirect measurements utilizing tracer gases (Broecker and Kaufman, 1970), and from *in situ* cuvette techniques (Coyne and Kelley 1972).

Aside from the human input of gases to the atmosphere and the sea, there is the unresolved set of questions about gases produced by natural processes in the sea, their genesis, and transport associated with their distribution and exchange across the ocean-atmosphere interface (Swinnerton et al., 1970; and Hahn, 1972). The processes involved in the interaction of these gases with other chemical constituents of the sea and with the marine biosphere are not well understood. In addition, rivers and streams are an important means of removing such gases as carbon dioxide from the continents and introducing them into the sea (Gordon et al., 1971; and Kelley and Hood, 1971).

Gases may be either chemically reactive or nonreactive in seawater. Carbon dioxide, sulfur dioxide, ammonia, nitrogen oxides, etc., are acid or base anhydrides and their air-sea transport mechanisms are more or less affected by their aqueous chemistry (Quinn and Otto, 1971). The class of nonreactive gases represented by methane, carbon monoxide, hydrogen, and helium have transport processes unaffected by an aqueous chemistry of this type. However, the nature of their roles as solutes may depend largely upon the formation of hydrates of clathrate structures in seawater, especially in cold and high pressure environments.

Because the gases whose balances are upset by man include both reactive and unreactive, the air-sea exchange mechanisms and rates of exchange should be examined for both classes. In particular, air-sea transfer coefficients of these gases should be studied. These data could then be used with field observations to calculate regional and mesoscale fluxes on a time-dependent basis. Global-scale fluxes in some cases where human and natural production figures are available are perhaps better approached by calculation (Craig, 1957; Revelle and Suess, 1957; Broecker et al., 1971; and Machta, 1972), but this approach might not be applicable to the question of the partitioning of biologically important gases (e.g. carbon dioxide) between the terrestrial biosphere and the oceans (Machta, 1972).

It has long been known that the sea surface, in general, is not in equilibrium with the atmosphere with respect to carbon dioxide and oxygen, although the departure is not large for oxygen (Craig, 1957). The greater carbon dioxide disequilibrium is related to its lower rate of exchange with the atmosphere. Of basic importance in any attempt

at estimating the regional air-sea exchange of any of the gases is a knowledge of the spatial and temporal variations in these air-sea disequilibria in surface seawaters, together with the respective transfer coefficients for the gases as functions of observable variables.

Much research remains to be conducted on the chemically reactive gases to elucidate the processes governing their distributions, and most importantly, the kinetics of their rate controlling reactions. Of classical importance is dissolved oxygen, which has been measured in the oceans to a tremendous extent, yet whose reaction kinetics have been directly measured only recently (Packard, 1971), although indirect inferences have been made for decades.

Many other gases eventually will prove increasingly important in studies of the oceans, including man's impact upon them. Examples include methane, relevant to petroleum exploration; carbon monoxide, relevant to undersea work and habitation; and nerve gas, relevant to waste disposal at sea. We know little of the kinetics of the rate controlling mechanisms governing the steady state and transit concentration levels of these gases in the oceans.

DETERMINATION OF THE FLUXES OF ORGANIC MATTER IN THE MARINE ENVIRONMENT

Organic matter in all its manifestations plays an important part in marine chemistry (see pp. 45). The formation of organic tissue involves the uptake of elements from the aqueous medium into discrete packages, which may become enriched in those elements by many orders of magnitude. An extreme example is the enrichment of polonium by a factor of 2×10^6 in certain organs of the North Pacific albacore (Folsom et al., 1972). Both during life and after the death of the organisms, dissolved and particulate organic and inorganic constituents are produced that continue to redistribute chemicals in the ocean. This redistribution may be active by scavenging chemicals from the water, or passive by decomposing, settling, and being carried along with the water. Understanding the fluxes of organic carbon, therefore, aids in the understanding of the distribution of many other elements and compounds, for example, heavy metals, DDT, and radioactive material from fallout.

Organic matter not associated with living organisms in the sea exceeds the amount of all living matter on earth by a factor of ten. Yet we do not know the chemical composition of most of this material, nor its rate of passage through the ocean. Since most of the organic matter is formed in the upper layers of the ocean, the rate of passage of the large amount of dead organic matter through the ocean depends critically on the recycling efficiency of the upper layers if a steady state is maintained.

Similarly, the rate of injection into the deep sea of those chemical constituents that "travel" in association with organic matter depends critically on the fraction of organic matter not oxidized in the upper layers. Therefore, important questions to be answered are as follows:

1. What is the recycling efficiency (ratio of oxidation to production) in the upper layers and how does it vary with depth, geographic position, and season?
2. What are the chemical and physical forms of organic matter injected into the deep sea?
3. At what rates are they injected.
4. What are the modes and rates of their interactions with one another and with the inorganic constituents?
5. What is the rate of oxidation of organic matter in the deep sea?
6. What quantities and what forms of organic matter reach the bottom?
7. How much is oxidized or solubilized at the bottom?
8. What is the rate of loss of carbon to the sediment?

Some of these questions can be answered by stable and radioactive isotope studies (e.g. carbon-13 and carbon-14) coupled with measurements of concentration changes in inorganic and organic phases. Others require sophisticated methods of organic analyses, of which some are available and others are being developed or need to be developed.

DETERMINATION OF THE FLUXES OF NOBLE GASES, INCLUDING RADON, AND LOW-MOLECULAR-WEIGHT ORGANIC GASES FROM THE SEDIMENTS INTO THE OVERLYING WATERS

What effect do the dissolved gases in ocean water have on life processes and how are they related to boundary conditions for models involving advective and convective mixing in deep waters? What are the diagenetic processes in marine sediments, including the formation of gases in sediments? These are fundamental questions yet unanswered. There is ample indirect evidence for the diffusion of noble gases from the sedimentary column to the overlying waters. Helium, produced in the earth's crust as a result of radioactive decay of isotopes of the uranium and thorium series, is found in higher concentrations in deep seawater than expected from solution of air. Further, there appears to be diffusion of noble gases in the sedimentary column as a consequence of thermal gradients. Quantitative measurement of fluxes of gases such as the noble gases are yet to be made, even though such numbers would provide important boundary conditions for models of the mixing and movements of deep waters.

Low-molecular-weight organic molecules such as methane and carbon dioxide are produced during the microbiological decomposition of organic matter, but few measurements of these gases have been made in the sedimentary column. Their presence in the overlying waters could affect life processes in them. An inventory of such gases and flux calculations should be made, for in addition to contributing to the properties of the overlying waters as mentioned above, it is postulated that layers of gases (possibly as clathrates) are responsible for certain strong acoustic reflectors observed in sediments.

The recent development of *in situ* interstitial water samplers allows for measurements of these gases dissolved in the interstitial waters in the top of the sedimentary column, and makes possible the calculation of fluxes. The methods for the analysis of these gases by mass spectroscopy and by gas chromatography are well developed. However, sampling devices for deeper portions of the sedimentary column still need to be developed.

Session C

Impact of Life Processes on the Chemistry of the Ocean

Dr. Francis A. Richards, Discussion Leader

INTRODUCTION

In identifying areas of research interest within the indicated area of chemical oceanography, a systematic discussion is presented, evaluating progress in four stages:

- Inventory of chemical variables altered by life processes
- Processes, rates, and mechanisms of those processes
- Synthesis with knowledge from other areas and disciplines
- Applications, prediction, and impacts.

In oceanography the inventory step has always had to await suitable analytical methods, but a scientific *raison a faire* has generally preceded the development of those analytical methods. As an example, Brandt (1899) suggested the importance of phosphorus and nitrogen compounds in limiting the productivity of the oceans, but analytical methodology appropriate to the problem was not developed until the early 1920's. Thus, although one cannot safely assume that the distribution of any specific constituent is unimportant to life processes and vice versa, areas of more probable importance can be identified.

Progress in chemical oceanography has produced inventories of some constituents that are adequate for the solution of many oceanographic problems, but there are many biologically altered and biologically important variables of which there is little or no knowledge. For example, repeated references are made to chelating materials that are almost wholly unidentified and yet are probably biologically highly significant. There are essentially no adequate analytical methods for determining these materials and no start on inventories of them. On the other hand, continued observations of many of the variables altered by life processes such as dissolved oxygen and the major nutrients that are made on a routine basis and continue to enrich their inventories.

It is evident that the inventory of chemical variables includes the problems of chemical speciation, particularly matters of complexation, chelation, and ligand formation. For example, the coordination of

metals with inorganic ions and organic ligands is certainly critical to the biological availability of the metals. These coordinations are in turn altered by changes brought about by biological processes, such as pH changes accompanying photosynthesis and respiration, and by biologically produced chelators.

The development and application of appropriate analytical methods is a necessary prerequisite to the development of inventories of chemical variables. Many sophisticated, sensitive, rapid, and automatic analytical methods have been developed in recent years, and we can now estimate the levels of many constituents of seawater that were unknown a few years ago. Nonetheless, the need for new techniques continues, especially in areas of biologically active substances, chelating agents, and the specific estimation of chemical species—particularly in reference to the state of metals in solution. Advances in qualitative organic analysis seem urgently needed.

Our understanding of the biological processes that alter the chemistry of the ocean, their mechanisms and their rates, tends to lag behind the inventory of chemical variables. Good progress has been made in some areas. The changes in dissolved oxygen, carbon dioxide, and the concentration of nutrients during photosynthesis and respiration are reasonably well understood and correlated. The complications of the additive effects of these life processes and of advection and diffusion on local changes in concentrations are sometimes amenable to explanation and modeling. With the advent of routine methods that yield inventories of chlorophyll, the phytoplankton biomass responsible for photosynthesis could be systematically estimated and limits could be placed on the photosynthetic potential of phytoplankton populations. The introduction of the carbon-14 method for estimating rates of photosynthesis and extensive studies of the photosynthetic process (generally not carried out by oceanographers) have provided considerable insight into the mechanism of this basic process.

It is probably the exception rather than the rule to have a good working knowledge of the biological processes that produce measurable changes in the chemistry of the ocean. Historically, the changes more often have been measured, and from them reconstruction of the biological processes producing those changes has been attempted. In some cases, one can now chemically characterize or estimate the potential of a biomass to carry out a biochemical process (through enzyme activity assays), and following the research required to relate the biochemical potential and the pertinent environmental parameters, one can estimate *in-situ* rates of processes, such as metabolic oxygen consumption. It is probably accurate and pertinent to point out that the evaluation of advective, diffusive, and biological terms in the equation for the local time change in chemical variable has always proved too complex to

make possible the general application of the equation. It is, therefore, necessary to seek other means for evaluating rates of biochemical changes in the oceans. In some instances, water masses can be isolated or identified and physically traced to give, when coupled with the proper chemical observations, rates of change, but these cases are few and far between, and generally this approach is not useful for determining reaction rates in the open ocean.

An understanding of the ocean cannot result from knowledge, however complete, of the chemical makeup of the ocean alone. The physics, biology, geology, and chemistry are so intimately intertwined that the amalgamation of knowledge from all these fields is essential to understanding the impact of life processes on the chemistry of the ocean. This is probably well understood by chemical oceanographers, but the synthesis of knowledge from such fields as biochemistry, organic chemistry, physical chemistry, and radiochemistry will be essential in applying chemical knowledge to the solution of important chemical problems. The impact of man's activities on the chemistry, biology, and geology of the ocean cannot be assessed or predicted without the application of such knowledge. It is also pertinent to point out that the converse is true for biology and geology, as has already been indicated in the Preface of this document. The short- and long-term effects of pollution on marine organisms, for example, will be the results of complex interactions among water, biota, and sediments.

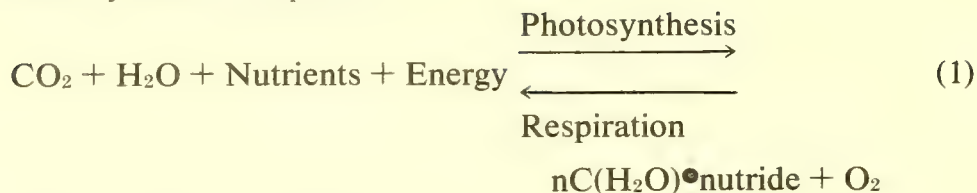
The ultimate goal for research is to apply our knowledge to the prediction of changes in the ocean, the possible control of those changes, and predicting the impact that biological events, stimulated naturally or artificially, will have on the chemistry of the oceans. One attempt has been made to identify areas of research that will increase our ability finally to predict and apply the impacts of life processes on the chemistry of the ocean.

IMPACT OF LIFE PROCESSES ON THE MAJOR CONSTITUENTS

For the purposes of this discussion, the major ionic constituents in seawater are those whose concentrations are at least 1 mg/liter and include chloride, sodium, sulfate, magnesium, calcium, potassium, bicarbonate, bromide, borate, strontium, and fluoride ions.

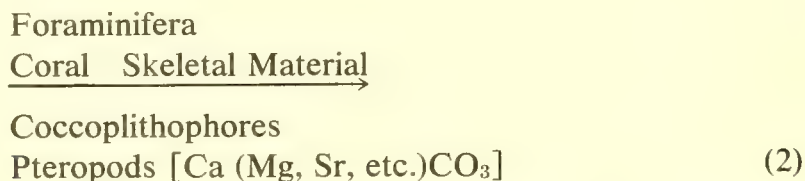
Life processes in the sea fall broadly into the categories of photosynthesis and respiration, where the latter includes the consumption of organic material as food by the various trophic levels of the food web. Although they might also be listed as respiratory processes, the formation of skeletal material by organisms in the sea and sulfate reduction are important life processes that have an impact on the major constituents. The processes listed above may be shown diagrammatically as follows:

i. *Photosynthesis-Respiration*



ii. *Skeletal Mineral Formation*

Organic Activity + Ionic Constituents



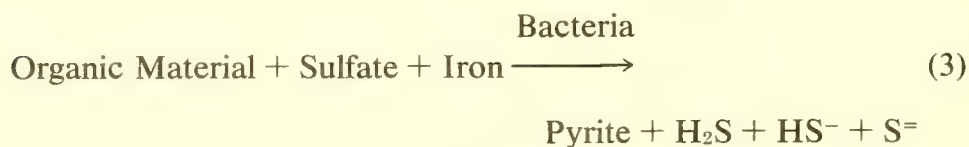
Minor Minerals

Barite (BaSO₄)

Celestite (SrSO₄)

Phosphorite (Ca₂PO₄F)

iii. *Bacterial Activity in Anoxic Water and Sediments*



Dissolved inorganic carbon is the only one of the major constituents (as defined) that is directly influenced by photosynthesis and respiration. The decrease in carbon dioxide in surface water caused by photosynthesis and the increase in carbon dioxide in intermediate and deep waters caused by respiration are routinely measured as part of many investigations and are relatively well understood.

In skeletal mineral formation, biological activity acts to bring about the formation of minerals that are near saturation in the sea. The reasons for the formation of a specific mineral in preference to another (i.e. high magnesium calcite over aragonite, etc.) are not well understood, but may be attributed to the amino acid or other organic makeup of the organisms. Since calcium carbonates are "sinks" for magnesium and strontium as well as for calcium and carbon, a change in the species of carbonate-depositing organisms may result in a change in the relative amounts of magnesium, strontium, and other elements being removed through geologic time.

Similarly, phosphorites are the result of organic activity in areas of upwelling. Recent evidence (Kolodny and Kaplan, 1970) indicates that

phosphorites have not been deposited for the last 100,000 years, and so this mechanism for the removal of calcium and fluoride is not active at the present time.

Sulfate reduction by bacteria and the formation of pyrite, particularly in deltaic sediments, is apparently the major life process that significantly changes sulfate concentrations in the sea over long time periods (Berner, 1971). Further studies of this important "sink" are necessary for a total understanding of the impact of life processes on the major constituents.

In considering the impact of life process on the major constituents, the inverse relationship, that is, the effect of the major constituents on life processes, should not be neglected. Questions remain concerning the changes in the chemical composition of the ocean with time, whether or not life processes had a part in changing the concentrations of the major constituents, and changes in inputs and sinks for the major constituents. These are all chemical oceanographic research areas requiring further investigation.

IMPACT OF LIFE PROCESSES ON HEAVY METALS

Heavy metals, important trace components of the ocean, may function in both the regulation and stimulation of biological processes. Seven metals (Mn, Cu, Zn, Mo, Co, Mg, and Fe) have known biological functions and are required in varying concentrations for growth and metabolism of all organisms. Of this group, copper and zinc have been found in toxic concentrations in the marine environment. Other heavy metals (including Sb, As, Pb, Cd, Cr, Hg, Ni, Ag, Sn, Se, and V) are found in organisms in concentrations that are high in comparison to the surrounding medium (Brooks and Rumsby, 1965). Many of these elements are highly toxic; lead, chromium, mercury, selenium, silver, and antimony have been identified as agents of the greatest environmental concern. Perturbations to the natural flux of trace elements into geochemical cycles are imposed by man's activities, and these are important to ecosystem functions. Natural control of ecosystems may well depend upon synergism and antagonism of heavy metal interactions, and relatively small perturbations caused by man may overload normal cycles and temporarily drive the system in a nonequilibrium direction. Uncontrolled stresses may drive the system beyond its ability to recover and could result in long-term or permanent damage.

Contemporary State of Knowledge

Our knowledge of the distribution, chemical forms, and fate of the trace metals in the oceans is inadequate to relate their chemistry to

biological processes involving stimulation, control, genetic changes, or toxicity. Little information is available even as to the total amounts of some elements such as antimony, cadmium, chromium and selenium. Probably copper, zinc, and iron have had more study than any other heavy metal and, although there is some evidence on their chemical speciation, there is no information on the importance of a given chemical species to a biological process. There is also little certain knowledge of the rates of interchange between chemical species of this group in the environment. There is evidence (Button, 1971) that the level of copper in ocean water (about 3 $\mu\text{g}/\text{liter}$) decreases the assimilative capacity of a laboratory yeast culture, unless some complexation occurs. The problem of "good" and "bad" ocean waters is thought to be closely related to trace metal complexation, which converts toxic forms, such as Cu^{+2} , to nontoxic ligand-bound forms. Data now being obtained on many of the heavy metals in the oceans will no doubt enhance our knowledge of the distribution of the specific chemical forms being examined, but they will have limited value in assessing their role in biological processes, the importance of the various chemical species to those processes, or the dynamics of the coastal processes that largely determine the fate of heavy metals in the ocean (National Academy of Sciences, 1971a). Increased research related specifically to the biology, biochemistry, chemical oceanography, and geochemistry of heavy metals in the ocean environment is required to gain an understanding of the effect of biological processes on trace-metal chemistry, and conversely, the chemistry of trace metals on biological processes.

Processes, Rates, and Mechanisms

A process that influences the heavy metal concentration of the oceans is the biological removal of oxygen from the sediments, which leads to the production of hydrogen sulfide and precipitation of insoluble heavy metal sulfides or the solubilization of elements such as iron and manganese. The rates of such removal, the status of the equilibrium, and the mechanisms of chemical and biological cycling in the sediments and through the sediment-water interface are subject of great importance in heavy metal chemistry.

The biota concentrate many heavy metals relative to their environment. Some of these elements have no apparent biological function, and it appears that the organisms have little capability for selective uptake or excretion. Such metals may not be toxic to the host organism, such as zinc or copper in oysters, but they may be passed up the food chain to higher organisms, including man.

Concerns about heavy metals in the environment often arise from a lack of understanding of the effects of perturbations on the natural

system imposed by man-made additions. Although it appears that the recent social concern with open-ocean pollution from these sources was not fully justified, local regions can be subjected to trace-metal contamination and associated environmental hazards. One of the serious problems is that of assessing the increase of trace metals in the marine environment because so little is known of their natural variations. Further complication arises from the geochemical dissimilarity of fluvial, estuarine and coastal regions by the dependency of organisms on trace metal availability, from the chemical forms of the metals in the water, and from the presence of other antagonistic or synergistic elements. Perspective can be gained of man's relative influence on trace-metal additions to the environment by comparing man-induced with natural inputs (Table 4). It is evident that man plays an important part in the mobilization of many of the heavy metals of concern. Fortunately, the coastal region, because of the intimate sediment-water interaction, appears best able to absorb excessive heavy metal input.

TABLE 4
Annual Rates of Mobilization

Element	Geologic Rate (G) (10 ³ metric tons)*	Man-Induced Rate (M) (10 ³ metric tons)†	Ratio M/G
Tin	1.5	166	110
Antimony	1.3	40	31
Lead	180.	2,330	13
Iron	25,000.	319,000	13
Copper	375.	4,460	12
Zinc	370.	3,930	11
Molybdenum	13.	57	4.4
Manganese	440.	1,600	3.6
Mercury	3.	7	2.3
Silver	5.	7	1.4
Nickel	300.	358	1.1

*Bowen (1966).

†United Nations (1968).

The influence of biological processes on the chemical state of trace metals in ocean water is not clear. However, the indirect influence is probably profound, because the organic matter that is responsible

for much of the complexing of metals in seawater is biologically derived. The organic moiety involved in complexing is not generally known; however, zinc has been found associated with a fulvic acid type of residue in seawater (Hood, 1967), and part of the copper in some waters is extractable in organic solvents (Slowey et al., 1967). Variable fractions of copper, manganese, and zinc occur in nondialyzable forms implying organic complexation (Slowey et al., 1971).

Modeling

Modeling of the distribution of heavy metals in the ocean has had limited success because the basic knowledge indicated above is lacking (also see pp. 27). The construction of models should be encouraged—but only after our understanding of their interactions with the biota is improved.

Future Efforts

The most clearly identified problem in relating biological systems to the chemistry of heavy metals in the ocean is that of chemical speciation and the effects of these species in controlling or stimulating biological activity. Not until we are aware of the chemical form in which heavy metals interact with biological membranes and are involved in vital life processes, can we obtain useful working models of the manner in which biological processes are controlled by heavy metals or provide detoxification systems against their deleterious effects.

The complexation of heavy metals with organic molecules has been limited. The source and structures of the organic portion, the stability of such complexes, and the availability of these complexes to biological systems need careful investigation. The attack must be coupled with biological experimentation that is sensitive to ultrasmall quantities of added trace elements, but this approach must await development of suitable techniques for it to be successful.

Studies of the spatial and temporal distributions of heavy metals in the ocean are needed, particularly near coasts. These studies should identify the chemical species, ratios of dissolved to particulate matter, association with sediments, and (where possible) the rate of movement between phases. The hypothesis should be carefully tested that sediment removal controls heavy-metal concentrations in the water column at the coastline.

IMPACT OF ORGANISMS ON MARINE ORGANIC CHEMISTRY

The organic chemistry of the marine environment is extremely complex. The ocean presumably contains most, if not all, of the compounds

that are formed by marine organisms. In addition, there are products of *in-situ* chemical reactions and natural materials derived from atmospheric sources. To an increasing degree, the sea contains residues of fossil fuels and synthetic organic compounds. The organic components of the marine environment interact with its other constituents through continuous destruction, new synthesis, and exchange with the atmosphere, the biosphere, and the lithosphere.

We can now begin to describe partially the composition of organic matter dissolved in seawater (DOM; 0.2 to 1.0 mg/liter), because of recent advances in analytical techniques, such as the combination of mass spectrometry with gas chromatography. The question of whether or not DOM from various locations and depths is the same can now be attacked. The bulk of this material may have a fairly simple structure, but this seems unlikely. It has been suggested that DOM is a polymer-like material condensed from amino acid and sugar subunits. Specific research is needed to determine what soluble polymers exist in seawater.

Dissolved organic matter requires more study for the following reasons:

- It is the largest reservoir of organic matter in the sea and one of the largest on earth.
- It probably modifies the chemical and biological properties of other seawater components, especially the trace metals.
- It may serve a function for marine organisms.
- It may be of use to man (e.g., drugs from the sea).

Regional studies of the organic chemistry of a few complex systems can increase our understanding and allow us to advance to larger systems. Intensive studies should be fruitful in oceanic areas where processes are relatively more rapid, such as

- Polar areas where the chemical character of water masses is continually changed.
- Continental margins where biological processes and rapid sedimentation help control the makeup of the sea. This includes upwelling zones.

A study of the organic matter in marine sediments that have been deposited in the last one million years is needed. A chemical record of how life adjusted to ice ages may be recorded in the proteins and amino acids of carbonate shells, and the optical activity of these amino acids may provide a new dating technique. Although amino acid levels in carbonate deposits are low (~ 100 ppm), the analytical methods are well developed (gas-liquid chromatography and ion exchange). Using new colorimetric reagents, amino acids can be detected in seawater directly.

One aim of the marine chemist is to inventory the organic chemicals in the sea and to understand their origin, role, and fate in terms of oceanic processes. When correlated with data from other scientific disciplines, models of oceanic processes can be developed and tested.

Progress in the different areas of marine organic chemistry (Table 5) has been uneven. In some areas (synthesis and turnover by microorganisms; marine polymers) we lack much basic information. In other areas (marine lipids), existing knowledge may permit modeling marine processes in some regions.

The understanding of marine processes, and specifically of mechanisms and rates, is critically important to the further development and application of marine chemistry. The reaction rates and mechanisms determine the magnitude of the "standing crop" of organic compounds in the dynamic system of the sea and the magnitude of the impact of natural and synthetic materials on marine ecology. Rates and mechanisms

TABLE 5
Organic Compounds of the Marine Environment

Medium for Organic Compounds	Basic Questions	Urgent Research	Applications and Relevance
Bacteria, Fungi	Origin, composition, variability, role	Inventory needed Turnover and decomposition rates	Pollution baselines and control coastal and deep ocean disposal
	Selectivity and efficiency in transfer processes	Knowledge rudimentary	Reworking of organic matter in sediments and seawater
Phytoplankton	Origin, composition, variability, role	Some existing knowledge; extended geographic and compositional range	Pollution baselines; low-level effects of pollution; primary production of marine organic matter
	Selectivity and efficiency in transfer processes	Little known	Dynamics of food web
Zooplankton	Origin, composition, variability, role	Some existing knowledge; extended geographic and compositional range	Pollution baselines, low-level effects of pollution; intermediary in marine food web; transfer of organics
	Selectivity and efficiency in transfer processes	Little known	Dynamics of food web, population dynamics and migration
Higher food web	Origin, composition, variability, role,	Some existing knowledge, extended geographic and compositional range, chemotaxis	Pollution baselines, human nutrition, public health, aquaculture, recycling capacity
Sediments	Sources, composition variability, interaction	Little known in recent sediments, especially in deep ocean	Pollution baselines, identification of low-level pollution, preservation of organics, recycling capacity, modification of acoustic properties
	Preservation, destruction, new formation	Reaction mechanisms, rates and intermediates largely unknown	
Seawater, dissolved, and particulates, surface films	Origin, composition, variability, fate, and Residence-time	Little known, especially in deep ocean; predictive models: rates and mechanisms	Dynamic processes: physical oceanography; pollution baselines and control; air-sea interaction; remote sensing
Atmosphere	Origin, composition, variability, fate, and Residence-time	Little known; baselines needed	Air-sea interaction; global exchange of pollutants

need to be studied both in areas where we expect rapid turnover (interfaces between sea and air, seawater and fresh water, seawater and sediments, and water and particulates) and in areas of low reactivity, such as the deep sea, where waste materials may persist indefinitely.

Organic compounds in the sea interact with other components of the ocean in ways that require, in most cases, further study. Thus, certain organic compounds play a role in the speciation of inorganic ions and determine their availability; other compounds may mediate processes that affect the life cycles of organisms (chemotaxis). Therefore, marine organic chemistry relates directly to oceanic productivity and to the capability of the ocean to recover from perturbations.

The great complexity of the marine organic matter presents an analytical challenge. Much development is needed to insure clean sampling, sample preservation, and initial separation of the concentrates into type compounds. For some classes of compounds (e.g., lipids, amino acids, carbohydrates), adequate analytical techniques are available from related fields. In other areas (e.g., marine polymers such as humates, fulvates, alginates, metal complexes) progress still depends on the development of methods for rapid routine analysis during large-scale oceanographic studies.

Table 5 classifies the sites of organic matter in the sea; it states some basic questions and suggests research areas and applications that deal with the impact of life processes on the organic chemistry of the ocean.

LIFE PROCESSES AND NUTRIENT SUBSTANCES

Life processes in the ocean alter the composition of seawater, and the changes thus produced impart distinguishing characteristics to the water in which they take place. The perturbation of the chemical medium may be apparent and easily detectable by chemical means, or it may be subtle, but nonetheless biologically significant in a long or short time scale. The former kinds of changes have made possible one of the classical activities of chemical oceanography – the characterization and tracing of water masses in the ocean. Continued research in this field appears to be essential, not simply to improve our knowledge of fields of motion in the ocean, but to predict the effects of biologically induced chemical changes on processes (chemical, biological, physical, geological) downstream from the sites of the biological events. Among questions to be resolved are prediction of plankton blooms as the result of nutrient fertilization, the detoxification of metals by chelation, and the stimulation of growth processes by the injection of vitamins and other biochemically active substances into a water mass. The changes brought about by life processes on the chemistry of the ocean are important for

their causative and diagnostic potentials and can be identified as important research areas. The commonly recognized water mass characteristics, such as the original temperature-salinity relationships among the conservative and nonconservative properties such as O_2 , alkalinity, pH, silicate, etc., will continue to be useful water mass tracers. However, many other biologically imparted characteristics can be used to give us more detailed knowledge of fields of motion and, perhaps even more importantly, of the fate and effects of biologically active substances in the ocean—whether they be naturally produced or artificially introduced.

Water mass properties that may be important both in describing fields of motion and in predicting oceanographic environments are listed below

1. Departures in the ratios of the major constituents resulting from alkaline-earth uptake, sulfate reduction, and similar processes
2. Trace-element concentrations and the ratios of the various ionic and molecular species in which the trace elements occur
3. The ratios of biologically altered nutrient substances, e.g. C:N, N:P, P:Si, and the concentrations of particulate and organic carbon
4. The presence of biologically active materials probably will be detected in the immediate future by bioassays. It is evident that these substances, along with toxic materials, have important consequences.
5. Petroleum and the identification of petroleum fractions might give important clues as to the origin of water masses and their course through the oceans. Persistent synthetic chemicals may prove useful as tracers.
6. The use of dissolved O_2 as a water mass tracer is historical and well documented. In specific areas where nitrogen fixation or denitrification alters the nitrogen content, precisely determined N_2/Ar ratios should be useful tracers.
7. Alkalinity and pH have been shown to be useful in tracing upwelling waters, estuarine waters, and in evaluating biological changes in such waters.
8. Man-made radioactive isotopes were the first artificially introduced water mass tracers useful over wide oceanic areas. Changes in the ratios of stable isotopes concurrent with biological processes could also be useful in this connection.

The growth and composition of plankton and micro-organism populations are subject to chemical controls. In turn, these biological processes significantly alter the chemistry of the water through both obvious and subtle feedback mechanisms. Indeed, the two biological processes of primary production and microbiological degradation are fundamental to the chemistry of the sea by displacing the equilibrium of the system and by catalyzing reactions back toward equilibrium.

Early realization of the importance of nutrients (P, N, and Si) to primary production and the hope of a fairly direct link to locations of

fishery resources led to extensive surveys of spatial and temporal variations of these nutrients. Gross inventories have been defined on a world basis and gross rates of reaction rates have been measured, especially in favorably hydrographic situations where information about physical movement and mixing of water masses has been available. Global estimates of primary productivity have also been accomplished.

Recent mathematical modeling of microscopic processes coupled with careful experimentation at natural (low) levels of chemical constituents have produced unexpected and useful results (Droop, 1968; Sieburth, 1969; Button, 1971, 1972; Caperon and Meyer, 1972a,b; Thomas and Dodson, 1972). Instead of growth rates being simply related to water composition, such systems are quantitatively described by transport relations describing the simultaneous flux of several nutrients to the cell surface (up concentration gradients of $10^2 - 10^6$ by active transport mechanisms), back-diffusion relations of nutrients and organic waste products, and internal nutrient regulation of growth through kinetic enzyme relations, (Button, 1972). These models are fairly simple and can be handled by computer techniques. Network models of such systems are feasible. Such models should be used to guide the design of laboratory and field experiments.

Some early results may serve as an example of the type of guidance that can be expected. The low controlling levels of chemical constituents and the competitive nature of the membrane transport sites imply that very low concentrations of nutrients (and of antimetabolites such as arsenate, trace metals, etc.) must be considered simultaneously. Rates of backleakage of nutrients and of organic metabolites significantly affect water chemistry as well as the flux relations in the models. Differences in continuous and batch incubation results should be examined in regard to field methods. The models and their results should also be examined as aids in the design of experiments on the effects of pollution.

Nutrients and Dissolved Gases—The abundances of the nutrient salts, phosphate, silicate, nitrate, nitrite and ammonia, plays a major role in controlling the productivity of the sea. Previous research has been focused on the development of suitable analytical methods and the application of these methods to the definition of the temporal and spatial distribution of nutrients in the ocean. Much of this definition has been accomplished, and it is now time to focus research on the rates and regulation of those processes that control and determine the characteristics of the nutrient fields, to construct mathematical expressions to describe these processes, and to nest these expressions in a predictive mathematical model. The mathematical model cannot be constructed or verified from our present knowledge of the rates and regulation of these processes, and since this inadequate understanding

is the result of our inability to make real-time rate measurements, research should be focused on developing our capacity to make such rate measurements, analagous to our present ability to make real-time concentration measurements.

The rates that must be measured are those of nutrient uptake by plankton and nutrient release by bacteria and zooplankton. These processes are modulated by environmental factors such as light, temperature, and pressure, plus biological factors such as biomass, species, and age. Our ability to measure fluxes in and out of living particles is limited to incubation techniques that are based on questionable assumptions, that are not suitable for the study of time-dependent processes, and that are too slow to be compatible with real-time data acquisition systems. The use of enzyme analysis in oceanographic research can relieve this reliance on incubation techniques by substituting *in-vitro* techniques that are amenable to continuous chemical determination. The use of enzyme analyses to estimate rates of biochemical process depends on the identification of the enzyme system that regulates the process and the measurement of its *in-vitro* substrate transformation rate, i.e., its activity. These measurements are sensitive and fast, and when properly calibrated, are as accurate as the more classical *in-vivo* incubation approach.

In addition, the dynamics of consumption and production of oxygen, carbon dioxide, hydrogen sulfide, nitrogen, hydrogen and methane are also controlled by intracellular enzymes of marine organisms. As a result, real time measurement of the rates of these fluxes and their variation in time and space can only be realized by determining the activity of these enzymes. To implement this research we must:

1. Identify the enzyme or enzyme systems that control the utilization and the formation of PO_4^{3-} , NO_3^- , NO_2^- , NH_4^+ and SiO_2 . These will probably be phosphatases, nitrate reductase, intrite reductase, and glutamate dehydrogenase, which control the fluxes of P and N. The enzymes regulating silicate fluxes are not known.
2. Develop analytical techniques to measure the activity of these enzymes and automate and interface the analyses with existing computer-controlled data-acquisition systems.
3. Derive mathematical expressions for the regulatory mechanisms by which light, substrate level, temperature, and physiology control the activity of these enzymes.
4. Determine the pattern of variation of enzyme activities in the marine environment and relate it to changes of the nutrient fields and to the biological and physical parameters.
5. Construct both conceptual and mathematical models of the nutrient cycles and the processes that control them in:
 - a. Upwelling areas

- b. The deep-sea
- c. Oligotrophic open-ocean gyres
- d. The top 10 cm of the water column
- e. The near-bottom nepheloid layer
- f. The interstitial water of sediments.

Synthetic Organic Materials—Synthetic organic chemicals are substances produced from naturally occurring raw materials. They usually do not occur in nature, and are developed and produced for some chemical or physical property that makes them useful, or they are produced as by products.

The wide variety of plastics, synthetic fibers, and pesticides, such as the chlorinated hydrocarbon DDT and polychlorinated biphenyls are examples. Several hundred synthetic organic chemicals are being produced in multi-ton quantities (see Table 6).

In the manufacture, transportation and use of these materials a probably substantial, but unknown, fraction of the total is injected into the marine environment. Life processes have an impact on these materials and vice versa. In some cases they are biologically degraded, which can be useful in the disposal of unwanted substances. Because of their solubility in lipids, they may become more concentrated in organs and organisms as the trophic levels are ascended. It has become evident during the past few years that some of these synthetic chemicals have an impact on marine life that constitutes a potentially serious threat. Several recent workshops have drawn attention to this problem and suggested plans for major research efforts to evaluate their impact (SCEP, 1970; Ketchum, 1972; and National Academy of Science, 1971, b).

We are in a strong position to formulate and carry out specific research directed at specific problems. Several pollutants of global concern have been identified. DDT and its decomposition products and polychlorinated biphenyls are examples. Others may be identified. The factors that combine to yield a potentially significant pollutant are: high production rates by industry; resistance to degradation in the environment; a route of transfer such as atmospheric transport from source to site; significant biological uptake; and toxicity for some level of life. These factors also allow a research program to be defined. At the present time the research needs are as follows:

1. Measurements of the levels of suspected toxic materials should be made in water, biota, and sediments. This research may require only local studies for some pollutants, or it may need global studies for pollutants such as DDT and the PCBs. Analytical methods are available for such research.

TABLE 6
(National Academy of Sciences, 1971b)
Estimated Involvement of Organic Substances
with the Marine Environment

Organic Substances and Sources	World Production (million tons/yr)	Lost to Marine Environment through Man's Activities (million tons/yr)
<i>Petroleum</i> (1969)	1820 (Tanker transported 1180)	
Lost to the marine environment through man's activities		
Offshore oil production		0.5
Tanker operations		0.5
Other ship operations		0.5
Spills		0.2
Deliberate dumping		0.5
Refinery operations		0.35
Industrial and auto		<u>0.45</u>
Total		3.00
<i>DDT and Aldrin—toxaphene</i>		
Lost to marine environment	0.2	0.05
<i>Polychlorinated biphenyls</i>		
Lost to marine environment	0.05	0.005

2. Investigation of the pathways and rates at which known synthetic organic chemicals are disseminated and how they move through the ecosystem should be conducted.

3. Research is needed on the toxicity and biological impact of known levels of pollutants. Such studies should go beyond determining lethal levels of pollutants. The overall welfare of marine communities such as primary production rates or the genetic pool, may be greatly influenced by sub-lethal concentrations.

4. The fate of pollutants at the sites of final deposition and rates of degradation need to be determined and appropriate models developed.

HYDROCARBONS IN THE MARINE ENVIRONMENT

Occurrence, Formation and Degradation

Both recent, biosynthetic, and fossil hydrocarbons occur in the sea; the latter are observed increasingly along tanker routes of the open ocean and in coastal areas receiving chronic spills. We lack fundamental data on the residence times of hydrocarbons in the open ocean, on beaches, in bottom sediments, and in organisms. The degradation and solution processes that disperse and destroy hydrocarbons are unknown, as is how recent and fossil hydrocarbons move through the biosphere, the hydrosphere, and the marine food web.

A closely allied problem is understanding the diagenesis of organic matter in sediments that leads to hydrocarbon accumulation. Changes in organic matter with depth in sediments of inland seas of the geologic past have been studied, but there have been only limited studies of cores from the present continental margins and deep sea. These studies indicate that some of the conversion processes may be slower because of lower temperatures and that different products may result because of differences in amounts and type of organic matter in the open ocean and in inland seas. We need more definitive studies of the mechanisms and rates of change of organic constituents of open ocean sediments.

Hydrocarbon Gases

Inventories of hydrocarbon gases in waters and sediments have been made in selected marine environments, but little is known of the processes and rates of their formation, accumulation, and decomposition. Methane, ethylene, and propylene are commonly present in near-surface waters of coastal margins and inland seas. The methane probably originates from anaerobic decay of organic matter, and the low-molecular-weight olefins are believed to be metabolic byproducts of plankton growth, but there is no clear evidence of these processes. We need studies to define mechanisms and rates of hydrocarbon production from biota in both shallow coastal and deep sea environments.

In reducing waters and sediments methane, ethane, and propane are the dominant hydrocarbons produced. Although the production of methane by micro-organisms utilizing carbon dioxide and hydrogen is established, there is no evidence of how ethane and propane are formed.

Transport mechanisms resulting in the migration and accumulation of hydrocarbons in sediments and waters are also poorly understood. Hydrocarbons may migrate either as bubbles or as part of a solution by convection and diffusion. In the Black Sea, methane formed in sediments and bottom waters migrates through the anoxic to oxic

waters, where methane-oxidizing bacteria convert part of it to carbon dioxide. In the Red Sea, hydrocarbon gases (methane through the butanes) are brought up by hot springs in contact with organic sediment at depth. Major rivers carry dissolved methane from the continents to the oceans. The movement of hydrocarbon gases has been traced in a few specific areas, but little is known of fluxes in and out of the oceans.

Transport of dissolved hydrocarbon gases from more deeply buried, compacting sediments to permeable, near-surface beds is particularly important. A phenomenon of these accumulations is the formation of *gas hydrates* (solids resembling ice), with the approximate formula $\text{CH}_4(\text{H}_2\text{O})_6$. Methane hydrates form from 0° to 24°C and at pressures of 400 to 6000 psi (equivalent to a total water-sediment column of about 300 to 4667 meters). They are believed to be widespread in sediments of continental margins, where bottom temperatures and pressures are conducive to their formation. They can cause sub-bottom reflections because of the high velocity of seismic waves in the crystalline hydrate layers, which can reach thicknesses of 500 meters. We need to know more about the origin, occurrence, and distribution of these gas hydrate layers in sub-bottom sediments. Core barrels need to be built that can take and retain samples at their subsurface pressures. Such equipment is available from the oil industry, but it needs modification for research programs.

REDOX POTENTIAL, pH AND ALKALINITY

For some elements the formation and concentration of chemical species depend on biological processes that directly or indirectly alter the redox potential, the pH, and the alkalinity. These processes can be nonbiological, biological, or some combination of both.

Redox Potential

The oceans are in a dynamic state with respect to oxidation and reduction. There are significant differences in the redox environment of the surface in contact with oxygen in the atmosphere, the deep waters that bathe the sediments. In between are intermediate zones resulting from diffusion and advection, or the lack of them, and from varying biological activities. Most redox reactions in the oceans depend on the activities of the biota. Redox levels within microenvironments close to biological surfaces may differ from those in the macroenvironment. Marine organisms internally mediate redox reactions by acting as centers of variant oxidation potential (e.g., the photosynthesizing cell is a center of low pE, permitting the reduction of CO_2 to glucose).

Externally, changes in pH as a result of photosynthesis and respiration and the precipitation and solution of calcium carbonate may affect the rate of abiotic redox reactions.

Carbon, nitrogen, oxygen, sulfur, iron, and manganese are the main elements that participate in oceanic reduction-oxidation reactions. These “redox elements” and the principal redox reactions mediated by plants and microbes are summarized in Table 7 in a form which focuses on the chemical species associated with each biological process. These reactions play an essential role in the vitality and chemistry of the ocean and need to be investigated in more detail.

Direct measurement of Eh values in the ocean is complicated and limited by practical problems. Quantitative interpretation of the results has been disappointing and has given only a general picture of the redox level. A better understanding may be obtained by directing more effort to biochemical studies of electron transport systems of the organisms that mediate or catalyze the transfer of electrons between the oxidizing and reducing substances. Once we understand the fundamental roles of these processes and know their location and magnitude in the ocean, we will better understand the essential chemical fluxes in the marine ecosystem and the practical problems of corrosion and recycling of pollutants.

pH

The chemistry of the oceans depends on the indirect influence of the biological assimilation and sorption or secretion and excretion of compounds that react with elements in the water. For example, pH changes depend on the amount of carbon dioxide taken up or released during photosynthesis and respiration. Also, pH is influenced by the secretion and dissolution of calcium carbonate by marine plants and animals. Diurnal variations in the euphotic zone change the pH of the surface layers. These changes, although small in the water column, may be significant in micro-environments close to biological and particulate surfaces. They may be significant to the following:

1. Degree of protolysis of acids in solution: The distributions of carbonate species, borates, phosphates, sulfides, hydrous oxides of iron and aluminum, and organic acids are determined by pH.

2. Precipitation reactions: Biologically induced changes in the pH of seawater may result in the precipitation of species that are at or near saturation. The *coprecipitation* of other elements is an important secondary effect, e.g., coprecipitation of Sr^{+2} , Pb^{+2} , and Zn^{+2} with CaCO_3 .

3. Complexation: Since many complexing agents are also conjugate bases of weak acids, the degree and stability of complexes in solution depends on pH.

TABLE 7
Principal Plant and Microbially Mediated Redox Reactions

Element	Biological Process	Mechanisms (rates)	Impact (species)
Carbon	Photosynthesis	Green plants mediate the reduction of C to the higher free energy state	$\text{H}_2\text{O}, \text{CO}_2 \rightarrow \text{CH}_2\text{O}, \text{O}_2$
Oxygen	*Respiration/ Decomposition	Oxidation of organic matter mediated by microbial aerobic heterotrophs	$\text{O}_2, \text{CH}_2\text{O} \rightarrow \text{CO}_2, \text{H}_2\text{O}$
Nitrogen	Nitrate Reduction/ Transformation	Mediated by microbial nitrate reducers; organics are oxidized by nitrate ions	$\text{NO}_3^- \rightarrow \text{NO}_2$
Nitrogen	Denitrification/ Transformation	Mediated by microbial denitrifiers; organic compounds are oxidized by nitrate ions	$\text{NO}_3^- \rightarrow \text{N}_2$
Nitrogen	N_2 — fixation	Mediated by photosynthetic blue-green algae and other microorganisms	$\text{N}_2 \rightarrow \text{NH}^+$
Manganese	Mn — reduction (or Oxidation*)	Mn bacteria	$\text{MnO}_2 \rightarrow \text{MnCO}_3$
Iron	Fe — reduction (or oxidation*)	Fe bacteria	$\text{FeOOH} \rightarrow \text{FeCO}_3$
Carbon	Fermentation	Mediated by microbial fermentors	$\text{H}_2\text{O}, \text{CH}_2\text{O} \rightarrow \text{CH}_3\text{OH}, \text{H}^+, \text{HCO}$
Carbon	Methane Fermentation	Mediated by H_2 forming bacteria and methane bacteria	$\text{CH}_2\text{O} \rightarrow \text{CH}_4, \text{CO}_2$ $(\text{H}_2?) (\text{C}_2 \text{H}_4?)$
Sulfur	Sulfate reduction	Microbially mediated by sulfate reducers organic compounds are oxidized by sulfate ion	$\text{SO}_4^{2-} \rightarrow \text{HS}^-$
Nitrogen	*Nitrification	Microbially mediated by nitrogen oxidizing bacteria	$\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$
Sulfur	*Sulfide oxidation	Microbially mediated by sulfur bacteria and photosynthetic sulfur bacteria	$\text{HS}^- \rightarrow \text{SO}_4^{2-}$ $\text{H}_2\text{S} \rightarrow \text{S}$

*These reactions take place in oxygenated regions. The other reactions, with the exception of photosynthesis, generally occur in anoxic regions and are initiated in a sequentially decreasing order as the Eh decreases.

4. Rate of reaction for “redox” elements: The rates of reactions that are normally slow may be substantially increased, e.g., at the surface of algae during photosynthesis and at the surface of CaCO_3 crystals.

5. Determination of reaction products: pH may control products where alternate or sequential pH-dependent reactions take place.

6. Sorption: Sorption of an element by suspended particulate matter may be influenced by hydrogen ions, which compete for or modify sorption sites. The influence of pH on the degree of protolysis of the sorbing solute should also be considered.

7. Flocculation: The degree of incorporation of solutes may depend on the pH at which flocculation takes place.

There is no general agreement on how pH should be measured nor on the precision or accuracy of the results. There is further complication because pH varies if the water sample is brought to a different pressure and temperature during measurement. Careful studies of the technique of pH measurement and of the effect of temperature and pressure are needed. The development of *in-situ* pH measurements should give new understanding of this important nonconservative property of seawater.

Alkalinity

The major anions in seawater are chloride, sulfate, bromide, bicarbonate, carbonate, and borate. Only the latter three have any appreciable power as bases. Phosphate and silicates (i.e. H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , $\text{H}_2\text{SiO}_4^{2-}$ and H_3SiO_4^-) are moderately effective as bases, but are generally present in minor concentrations (<1 ppm) except in anoxic waters where sulfides (i.e. HS^- and S^{2-}) and ammonia may become appreciable. The total concentration of these “Lewis Bases,” in addition to the small excess of hydroxide ions, are referred to as the “alkalinity” of seawater—the capacity of seawater to neutralize the addition of a strong acid without an extreme change in pH. It is a property of seawater that prevents large disturbances to life processes in the ocean. Alkalinity may be at times a main variable in the chemical composition of seawater. The secretion of calcium carbonate shells by organisms and their subsequent dissolution seem to be the main factors influencing the alkalinity. Changes can arise from the complexing of carbonate species, boric acid volatility, biological production of organic matter and ammonia, and others. The ratio of alkalinity to the chlorinity (the specific alkalinity) varies significant with depth, in anoxic basins, near coasts, and in shallow tropical seas where calcium carbonate precipitates. A better understanding of the species contributing to the total alkalinity in different regions is needed. Moreover, since calcium carbonate is

present in all living things, a study of metabolic influences on the formation of calcium carbonate is important. A study of the impact of life processes on the calcium chemistry and alkalinity of seawater should be concerned with the biochemistry of the organism as well as the physicochemical influence of the medium. Finally, because of the many reactions that are influenced by pH, the buffering aspect of the alkalinity is important to the chemistry of seawater and its stability as a biological environment.

Impact of Life Processes on Radioactive and Stable Nuclides

Radionuclides in the ocean may be naturally occurring or manmade. Naturally occurring radionuclides are the cosmic-ray-produced species, such as carbon-14, hydrogen-3, beryllium-10, uranium-238, uranium-235, and thorium-232, and their many daughter products, such as thorium-230, radium-226, lead-2, radium-228, protactinium-231, etc. Manmade radionuclides consist of the fission and fusion products given off by nuclear-weapon tests, controlled nuclear reactors, and power generators. Some of the most important in the ocean are carbon-14, hydrogen-3, strontium-90, cesium-137, zinc-65, and plutonium-238 and 239 (see pp. 33).

Life processes are important in transporting many of these nuclides from surface into deep water. For example, "bomb" carbon-14 has been found in the tests of foraminifera at great depths in the sea. High levels of fission products have been found in fish caught in the open ocean, and these fish must be important agents for transporting these nuclides. (see pp. 33).

Life processes are important in transferring radioactive elements. For example, photosynthesis transfers "bomb" carbon-14 from inorganic to organic carbon in the marine ecosystem. Although life processes have a tremendous influence on radionuclides, the inverse relationship is as much, if not more, important, but these influences are poorly understood. Some fission products and plutonium may be concentrated to high and possibly deleterious levels in various organs of fish and higher organisms (Folsom, 1972). The effects of these radionuclides on organisms needs to be assessed.

The field of stable isotope geochemistry has an excellent record of providing answers to specific questions. For example:

1. Paleo-temperatures based on O^{18}/O^{16} ratios.
2. Sulfur dome origins based on S^{34}/S^{32} ratios.
3. Oil field and oil source bed correlation based on C^{13}/C^{12} ratios.
4. Water cycles based on O^{18}/O^{16} ratios.

Several parts of stable isotope geochemistry are now ready to yield important information:

1. N^{15}/N^{14} natural variations may provide valuable insight into the marine nitrogen cycle.

2. C^{13}/C^{12} ratios can suggest the kind of processes that put organic matter into marine sediments now and especially during the last two ice ages. These ratios can also help to demonstrate that different types of photosynthesis (at least two) are going on.

3. O^{18}/O^{16} data on dissolved O_2 can help explain the oxygen cycle in the sea.

Radionuclides in seawater are characterized by their extremely high dilutions, and when higher concentrations are encountered, it should always be suspected (and frequently is demonstrated) that life processes have been involved. Some of the most spectacular examples of trace-element accumulations have been demonstrated by following the uptake of radionuclides of certain metals by living systems. For example, the living interfacial region between seawater and certain brown algae accumulates concentrations of both natural polonium and artificial plutonium by orders of magnitude above ambient water; polonium-210 by 90,000-fold, and plutonium-239 by 3,000-fold (Wong et al. 1972). (See p. 65)

In the case of polonium, additional buildup occurs in specific organs of animals high in the tropic level. An extreme case is the 2.2×10^6 -fold buildup (over seawater) of polonium-210 in one organ of a tuna fish (Folsom et al. 1972).

Life processes may afford powerful tools for understanding the distributions certain trace elements in the ocean. Even information on major currents, and also information concerning mixing rates, can come from chemical and radiochemical inspections of concentration buildup in living systems. These often are most conveniently followed through their radioactive properties (Folsom et al. 1968, 1970, Hodge et al. 1972).

References

Anikouchine, W.A., 1967, Dissolved chemical substances in compacting marine sediment, *J. Geophys. Res.* 72(2), 505-509.

Apollonio, S., 1961, The chlorophyll content of Arctic sea-ice, *Arctic* 14, 197-200.

Apollonio, S., 1965, Chlorophyll in Arctic sea ice, *Arctic* 18, 118-122.

Assur, A., 1958, Composition of sea ice and its tensile strength, in: HAS-HRC. publ. 698, Arctic Sea Ice, pp. 106-138.

- Atkinson, G., M.O. Dayhoff and D.W. Ebdon, 1972, Computer modeling of inorganic equilibria in seawater, in: Marich Electrochemistry, Electrochemical Soc., N. J.
- Atkinson, L.P., 1972, Air bubbles in an oceanic mixed layer: Effect on gas concentrations and air-sea exchange, Ph.D. Thesis, Dalhousie University, Halifax, Nova Scotia.
- Bennington, K.O., 1962, Some chemical composition studied on Arctic sea ice, in: Ice and Snow: properties, processes and applications, W.D. Kingery, ed., Cambridge, Mass., M.I.T. Press, pp. 248-257.
- Ben-Yaakov, S. and I.R. Kaplan, 1971, Deep-sea *in-situ* calcium carbonate saturometry, *J. Geophys. Res.* 76(3), 722-731.
- Berger, W.H., 1967, Foraminiferal ooze: Solution at depths, *Science* 156, 83-85.
- Berner, Robert A., 1964, An idealized model of dissolved sulfate distribution in recent sediments, *Geochim. Cosmochim. Acta* 28, 1497-1503.
- Berner, Robert A., 1971, Principles of chemical sedimentology, McGraw-Hill Book Co., New York, pp. 240.
- Bezdek, H.F., 1972, Pressure dependence of high-frequency sound attenuation in the deep Pacific Ocean (abs.), *J. Acoust. Soc. Am.* 52, 173.
- Bezdek, H.F., 1973, paper to be presented at 85th Meeting of Acoust. Soc. Am.
- Bieri, R.H., 1971, Dissolved noble gases in marine waters, *Earth and Planetary Science Letters* 10(3), 329-333.
- Bjerrum, N., 1926, Investigations of Association of Ions, I., *Kgl. Danske Videnskab. Selskab* No. 9, 7.
- Bloch, M.R. and W. Luecke, 1972, Geochemistry of ocean water bubble spray, *J. Geophys. Res.* 77, 5100-5105.
- Bolin, B. and E. Eriksson. Changes in the carbon dioxide content of the atmosphere and sea due to fossil fuel combustion, The atmosphere and the sea in motion; Scientific contributions to the Rossby Memorial Volume 1959, B. Bolin, ed., New York, Rockefeller Inst. and Oxford Univ. presses, pp. 130-142.
- Bowen, H.J.M., 1966, Trace elements in biochemistry, New York, Academic Press, pp. 241.
- Brandt, K., 1899, Uber den Stoffwechsels im Meer. Komm, z. *Wissenschaft. Untersuch. Deutschen Meere in Kiel and d. Biologischen Anstalt*

auf Helgoland. *Wissensch. Meeresuntersuch.*, W.F., Abt. Kiel, Bd. 4, 213-230.

Brewer, P.G. and D.W. Spencer, 1970, Trace element intercalibration study, Technical Report (Ref. no. 70-62), Woods Hole Oceanographic Inst., pp. 63.

Broecker, W.S. and A. Kaufman, 1970, Near-surface and near-bottom radon results for the 1969 North Pacific Geosecs Station, *J. Geophys. Res.* 75(36), 7679-7681.

Broecker, W.S., Y-H Li, and T-H Peng, 1971, Carbon dioxide—man's unseen artifact, Impingement of Man on the Oceans, D.W. Hood, ed., New York, Wiley, pp. 287-384.

Broecker, W.S., 1971, A kinetic model for the chemical composition of seawater, *Quaternary Res.* 1, 188-207.

Brooks, R.R. and M.G. Rumsby, 1965, The biogeochemistry of trace element uptake by some New Zealand bivalves, *Limnol. Oceanog.* 10, 521-527.

Brown, C.W. and C.D. Keeling, 1965, The concentration of atmospheric carbon dioxide in Antarctica, *J. Geophys. Res.* 70(24), 6077-6085.

Button, D.K., 1971, Multiple substrate transport in dilute solution, Inst. of Marine Science, Report R-71-5, Univ. of Alaska, Fairbanks, Alaska.

Button, D.K., 1972, Personal Communication, Inst. of Marine Science, Univ. of Alaska, Fairbanks, Alaska.

Caperon, J. and J. Meyer, 1972a, Nitrogen limited growth of marine phytoplankton I, Changes in population characteristics with steady state growth rate, *Deep-Sea Res.* 19, 601-618.

Caperon J. and J. Meyer, 1972b, Nitrogen limited growth of marine phytoplankton II, Uptake kinetics and their role in nutrient limited growth of phytoplankton, *Deep-Sea Res.* 19, 619-632.

Carpenter, J.H., 1972, Problems in application of analytical chemistry of oceanography, Natl. Bur. Stds. Publ. 351, Analytical Chemistry: Key to Progress on National Problems, Proc. 24th Symp., Gaithersburg, Md., Ch. 7, 393-414.

Chave, K.E. and E. Suess, 1972, Calcium carbonate saturation in seawater: Effects of dissolved organic matter, *Limnol. Oceanog.* 15, 633-637.

Chave, K.E. and S.V. Smith, 1972, Inorganic cycles of calcium and carbon in the ocean, Tokyo Symposium 1970, in press.

- Chester, R., 1965, Elemental geochemistry of marine sediments, in: Chemical Oceanography, edited by J.P. Riley and G. Skirrow, Vol. 2, pp. 23-80, London, Academic Press.
- Clasby, R., R. Horner, and V. Alexander, 1972, Ecology and metabolism of sea ice organisms, Progress report to the National Science Foundation, Inst. of Marine Science, Univ. of Alaska, Fairbanks, Alaska, Report No. 772-6.
- Coleman, G.H., 1965, The Radiochemistry of Plutonium, NAS-NS-3058, pp. 102.
- Coyne, P.I. and J.J. Kelley, 1972, Equilibrium partial pressure of CO₂ in Arctic surface waters, paper presented at the Fall National Meeting of the American Geophysical Union, San Francisco, California, 4-7 Dec. 1972.
- Craig, H., 1957, The natural distribution of radiocarbon and the exchange time of carbon dioxide between atmosphere and sea, *Tellus* 9(1), 1-17.
- Craig, H. and R.F. Weiss, 1971, Dissolved gas saturation anomalies and excess helium in the ocean, *Earth and Planetary Science Letters* 10(3), 289-296.
- Crank, J., 1956, The Mathematics of diffusion, Oxford Univ. Press, Oxford, U. K., pp. 9-61, 121-246.
- Crease, J., 1962, The specific volume of seawater under pressure as determined by recent measurements of sound velocity, *Deep-Sea Res.* 9, 209-213.
- Cronan, D.S. and J.S. Tooms, 1969, The geochemistry of manganese and associated pelagic deposits from the Pacific and Indian Oceans, *Deep-Sea Res.* 16(4), 335-359.
- Culkin, F., 1965, The major constituents of seawater, in: Chemical Oceanography Vol. 1, pp. 121-161, J.P. Riley and G. Skirrow, ed., London Academic Press.
- Culkin, F. and R.A. Cox, 1966, Sodium, potassium, magnesium, calcium and strontium in seawater, *Deep-Sea Res.* 13, 789-804.
- Daly, F.P., C.W. Brown, and D.R. Kester, 1972, Sodium and magnesium sulfate ion-pairing: Evidence from Raman Spectroscopy, *J. Phys. Chem.* 76, 3664-3668.
- Del Grosso, V.A. and C.W. Mader, 1972, Speed of sound in seawater samples, *J. Acoust. Soc. Am.* 52, 961-975.

Drever, J.I., 1973, The magnesium problem, in: *The Sea*, Vol. 5, E.D. Goldberg, ed., New York, Wiley (in press).

Droop, M.R., 1968, Vitamin B₁₂ and Marine Ecology IV, The kinetics of uptake growth and inhibition in *monochrysis lutheri*, *J. Mar. Biol. Assn. U.K.* 48, 689-733.

Duce, R.A., J.G. Quinn, C.E. Olney, J.R. Piotrowicz, B.J. Ray and R.L. Wade, 1972, Enrichment of heavy metals and organic compounds in the surface microlayer of Narragansett Bay, Rhode Island, *Science* 176, 161-163.

Duursma, E.K., 1966, Molecular diffusion of radioisotopes in interstitial waters of sediments, Symp. Disposal of Radioactive Wastes into Seas, Oceans and Surface Waters, pp. 355-371, International Atomic Energy Agency, Vienna.

Duursma, E.K., 1970, Theoretical, experimental and field studies concerning diffusion of radioisotopes in sediments and suspended particles of the sea, Part B: Methods and Experiments, *Neth. J. Sea Res.* 4(4): 395-469.

Emmet, R.T. and F.J. Millero, 1973, The high pressure P-V-T properties of seawater—preliminary results, paper to be presented at 154th A.G.U. Meeting, Washington, D.C.

Fine, R., Dong-Ping Wang and F.J. Millero, 1972, The equation of state of seawater as determined from sound data, paper MM 12, 84th Meeting of Acoustical Society of America, Miami Beach, Florida.

Fisher, F.H., 1967, Ion-pairing of magnesium sulfate in seawater: determined by ultrasonic absorption, *Science* 157, 823.

Fisher, F.H., E. Yeager, J. Miceli and R. Bressel, 1972, Origin of the relaxation and absorption in seawater below 1 kHz, paper MM 8, 84th Meeting of Acoustical Society of America, Miami Beach, Florida.

Folsom, T.R., G.J. Mohanroa, K.C. Pillai and C. Sreekumaran, 1968, USAEC Fallout Program Quarterly Report, HASL-197, 95-203.

Folsom, T.R., C. Sreekumaran, N. Hansen, J.M. Moore, and R. Grisimore, 1970, USAEC Fallout Program Quarterly Report, HASL-217, 9-118.

Folsom, T.R., 1972, Modeling the upper North Pacific layers using Cs-137 and Pu-239, submitted to *Marine Chemistry*.

Folsom, T.R., K.M. Wong, and V.F. Hodge, 1972, Some extreme accumulations of natural polonium radioactivity observed in certain

oceanic organisms, paper presented at Natural Radiation Environment II Symp., Houston, Texas.

Garland, F. and G. Atkinson, 1973, Computer Simulation of Sound Absorption in Seawater, *J. Acoust. Soc. Am.* (in press).

Garrels, R.M., M.E. Thompson and R. Siever, 1961, Control of carbonate solubility by carbonate complexes, *Am. J. Sci.* 259, 24-45.

Garrels, R.M. and M.E. Thompson, 1962, A chemical model for seawater at 25°C and one atmosphere total pressure, *Am. J. Sci.* 260, 57-66.

Garrels, R.M. and F.T. MacKenzie, 1971, The Evolution of Sedimentary Rocks, New York, W.W. Norton and Co., p. 397.

Goering, J.J. and D. Wallen, 1967, The vertical distribution of phosphate and nitrate in the upper one-half meter of the southeast Pacific Ocean, *Deep-Sea Res.* 14(1), 29-33

Goldberg, E.D., 1965, Minor elements in seawater, in: Chemical Oceanography, J.P. Riley and G. Skirrow, ed., Vol. 1, London, Academic Press, pp. 163-196.

Goldberg, E.D., 1971, Atmospheric transport, in: Impingement of Man on the Oceans, D.W. Hood, ed., New York, Wiley, p. 75-88

Gordon, L.I., P.K. Park, S.W. Hager and T.R. Parsons, 1971, Carbon dioxide partial pressures in North Pacific surface waters: Time variations, *J. Oceanog. Soc. Japan* 27(3), 81-90.

Gordon, L.I., 1973, A study of carbon dioxide partial pressures in surface waters of the Pacific Ocean, Ph.D. dissertation, Oregon State Univ., Corvallis, 216 p.

Hahn, J., 1972, Nitrous oxide in air and seawater over the Atlantic Ocean, in The Changing Chemistry of the Ocean, Nobel Symposium 20, D. Dryssen and D. Jagner, eds. New York, Wiley, pp. 53-69.

Hardy, E.P., P.W. Krey, and H.L. Volchok, 1972, Global inventory and distribution of Pu-238 from SNAP-9A, USAEC HASL-250.

Hawley, J.E., 1973, Bicarbonate and carbonate association with sodium, calcium and magnesium at 25°C and 0.72 ionic strength, Ph.D. Thesis, Oregon State Univ., Corvallis, 66 pp.

Helgeson, H.C., 1971, Kinetics of mass transfer among silicates and aqueous solutions, *Geochim. Cosmochim. Acta* 35, 421-469.

Hodge, V.F., T.R. Folsom, and D.R. Young, 1972, Retention of fallout constituents in upper layers of the Pacific Ocean as estimated from

studies of a tuna population, IAEA Symp. on the Interaction of Radioactive Contaminants with the Constituents of the Marine Environment, Seattle, Wash. July 10-14, in press.

Holland, H.D., 1965, The history of ocean water and its effect on the chemistry of the atmosphere, *Proc. Natl. Acad. Sci.* 53, 1173-1182.

Hood, D.W., 1967, Chemistry of the oceans: some trace metal-organic associations and chemical parameter differences in top one meter of surface, *Environ. Sci. Tech.*, 1, 303-305.

Hurd, D.C., 1972a, Factors affecting solution rate of biogenic opal in seawater, *Earth Planet. Sci. Letters*. 15, 411-417.

Hurd, D.C., 1972b, Interactions of biogenic opal, sediment and seawater in the Central Equatorial Pacific, Ph.D. dissertation, Hawaii Inst. of Geophys. Ref. 72-22, Univ. of Hawaii, Honolulu, Hawaii.

Kanwisher, J., 1963, On the exchange of gases between the atmosphere and the sea, *Deep-Sea Res.* 10, 195-207.

Kelley, J.J., 1970, Carbon dioxide in the surface waters of the North Atlantic Ocean and the Barents and Kara Seas, *Limnol. Oceanog.* 15, 80-87.

Kelley, J.J. and D.W. Hood, 1971, Carbon dioxide in the Pacific Ocean and Bering Sea: Upwelling and mixing, *J. Geophys. Res.* 76(3), 745-752.

Kelley, J.J., L.L. Longerich, and D.W. Hood, 1971, Effect of upwelling, mixing, and high primary productivity on CO₂ concentrations in surface waters of the Bering Sea, *J. Geophys. Res.* 76(36), 8687-8693.

Kelley, J.J., 1972, Ozone in the Arctic atmosphere, *Pure and Applied Geophys*, Basel, Kirkner Verlag, in press.

Kester, D.T. and R.M. Pytkowicz, 1968, Magnesium sulfate association at 25°C in synthetic seawater, *Limnol. Oceanog.* 13, 670-674.

Kester, D.R. and R.M. Pytkowicz, 1969, Sodium, magnesium and calcium sulfate ion pairs in seawater at 25°C, *Limnol. Oceanog.* 14, 686-692.

Kester, D.R. and R.M. Pytkowicz, 1970, Effect of temperature and pressure on sulfate ion association in seawater, *Geochim. Cosmochim. Acta.* 34, 1039-1051.

Kester, D.R. and R.H. Byrne, 1972, Chemical forms of iron in seawater, in: Proceedings of the Conference on Ocean Manganese Deposits, Lamont-Doherty Geological Observatory.

Ketchum, B.H., 1972, *The Water's Edge: Critical Problems of the Coastal Zone*, Cambridge, Mass., MIT Press.

Kolodny, Y. and Kaplan, I.R., 1970, Uranium isotopes in sea floor phosphorites, *Geochim. Cosmochim. Acta* 34, 3-24.

Komhyr, W.D., E.W. Barrett, G. Slocum, and H. Weickmann, 1971, Atmospheric total ozone increase during the 1960's, *Nature* 232(5310), 390-391.

Lafon, G.M., 1969, Some quantitative aspects of the chemical evolution of the oceans, Ph.D. Thesis, Northwestern University, Evanston, Illinois.

Lepple, F.K. and F.J. Millero, 1971, The isothermal compressibility of seawater near one atmosphere, *Deep-Sea Res.* 18, 1233-1254.

Lerman, Abraham, 1971, Time to chemical-steady-states in lakes and ocean, *Non-equilibrium Systems in Natural Water Chemistry*, Advances in Chemistry Series 106, ACS, Washington, D.C., pp. 30-76.

Lieberman, L., 1949, Sound propagation in chemically active media, *Phys. Rev.* 76, 1520-1524.

Lieberman, L., 1957, Air bubbles in water, *J. Appl. Phys.* 28, 205-211.

Luce, R.W., R.W. Bartlett, and G.A. Parks, 1972, Dissolution Kinetics of Magnesium Silicates, *Geochim. Cosmochim. Acta* 36(1), 35-50.

Lyman, J. and R.H. Fleming, 1940, Composition of seawater, *J. Mar. Res.* 3, 134-146.

Machta, L., 1972, The role of the oceans and biosphere in the carbon dioxide cycle, in: *The Changing Chemistry of the Oceans*, Noble Symposium 20, D. Dyrssen and D. Jagner, eds. New York, Wiley, pp. 121-146.

MacIntyre, F., 1972, Flow patterns in breaking bubbles, *J. Geophys. Res.* 77, 5211-5228.

MacKenzie, F.T. and R.M. Garrels, 1966a, Silica-bicarbonate balance in the ocean and early diagenesis, *Sed. Pet.* 36, 1075-1084.

MacKenzie, F.T. and R.M. Garrels, 1966b, Chemical mass balances between rivers and oceans, *Am. J. Sci.* 264, 507-525.

Manheim, F.T., 1970, The diffusion of ions in unconsolidated sediments, *Earth and Planetary Sci. Ltr.* 9, 307-309.

Medwin, H., 1970, *In situ* acoustic measurement of bubble populations in coastal ocean waters, *J. Geophys. Res.* 75, 599-611.

- Meguro, K., K. Ito and H. Fukushima, 1967, Ice flora (bottom type): A mechanism of primary production in polar seas and the growth of diatoms in sea ice, *Arctic* 20, 114-133.
- Mero, J.L., 1965, *The Mineral Resources of the Sea*, Amsterdam, Elsevier. 312 p.
- Millero, F.J., 1969, The partial molal volumes of ions in seawater, *Limnol. Oceanog.* 14, 376-385.
- Millero, F.J., 1971, The molal volume of electrolytes, *Chem. Rev.* 71, 147-176.
- Millero, F.J., 1971a, The physical chemistry of multi-component salt solutions, in: *Biophysical Properties of Skin*, H.R. Elden, ed., Wiley and Sons, Inc. New York, pp. 329-337.
- Millero, F.J., 1971b, Effect of pressure on sulfate ion association in seawater, *Geochim. Cosmochim. Acta* 35, 1089-1098.
- Millero, F.J. and R.A. Berner, 1972, Effect of pressure on carbonate equilibria in seawater, *Geochim. Cosmochim. Acta* 36, 92-88.
- Millero, F.J., J.H. Knox and R.T. Emmet, 1972, A high-precision, variable-pressure magnetic float densimeter, *J. Soln. Chem.* 1, 173-186.
- Millero, F.J., L.D. Hansen and E.V. Hoff, 1973, The enthalpy of seawater from 0 to 30°C and 0 to 90‰ salinity, *J. Mar. Res.* (in press).
- Millero, F.J., 1973a, Seawater as a multicomponent Electrolyte Solution, in: *The Sea*, Vol. 5, E.D. Goldberg ed., New York, Wiley, (in press).
- Millero, F.J., 1973b, The physical chemistry of seawater, *Ann. Rev. Geol. Geophys.* (in preparation).
- Millero, F.J., 1973c, Theoretical estimates of the isothermal compressibility of seawater, *Deep-Sea Res.* (in press).
- Millero, F.J., 1973d, Seawater—a test for multicomponent electrolyte solution theories I. The apparent equivalent volume, expansibility and compressibility of artificial seawater, *J. Soln. Chem.* (in press).
- Miner, W.N., 1964, Plutonium, *Understanding the Atmos. Series*, USAEC Technical Information Division, Oak Ridge, Tenn. p. 35-37.
- Miyake, Y. and Y. Sugimura, 1968, Plutonium content of the western North Pacific Waters, *Papers on Meteorology and Geophys.* Tokyo 19(3), 481-485.

Morris, T.C. and W. Stumm, 1967, Redox Equilibria and Measurements of Potentials in the Aquatic Environment, in: Equilibrium Concepts in Natural Water Systems, Advances in Chemistry Series 67, ACS, Washington, D.C., pp. 270-285.

National Academy of Sciences, 1971, Marine Chemistry, Washington, D.C., 60 pp.

National Academy of Sciences, 1971, Marine Environment Quality, Report of a special study held under the auspices of the Ocean Science Committee, NAS-NRC Ocean Affairs Board, Washington, D.C., 107 pp.

Noshkin, V.E. and V.T. Bowen, 1972, Concentrations and distributions of long-lived fallout radionuclides in open ocean sediments, IAEA-SN-158-45. IAEA Symp. on the Interaction of Radioactive Contaminants with the constituents of the Marine Environment (in press).

Olafson, J.H. and K.H. Larsen, 1963, Plutonium, Its Biology and Environmental Persistence, in Radioecology, New York, Reinhold, pp. 636-639.

Packard, T.T., 1971, The measurement of respiratory electron-transport activity in marine phytoplankton, *J. Mar. Res.* 29(3), 235-244.

Pales, J.C. and C.D. Keeling, 1965, The concentration of atmospheric carbon dioxide in Hawaii, *J. Geophys. Res.* 70(24), 6053-6076.

Peterson, M.N., 1966, Calate: rates of dissolution in a vertical profile in the central Pacific, *Science* 154, 1542-1544.

Pillai, K.C., R.C. Smith and T.R. Folsom, 1964, Plutonium in the marine environment. *Nature* 203, pp. 568-571

Piro, A., M. Bernhard, and M. Verzi, 1972, The Interaction of Radioactive Contaminants with the Constituents of the Marine Environment, in: IAEA Symposium, Seattle (in press).

Pytkowicz, R.M., 1965, Rates of inorganic calcium carbonate precipitation, *J. Geol.* 73, 196-199.

Pytkowicz, R.M., 1972, The chemical stability of the oceans and the CO₂ system, in: Proc. 12th Nobel Symp. D. Dyrssen and D. Jagner, ed., Stockholm, Plmgvist and Wiksell, pp. 147-152.

Pytkowicz, R.M. and D.R. Kester, 1969, Harned's rule behavior of NaCl Na₂SO₄ resolutions explained by an ion association model, *Am. J. Sci.* 267, 217-229.

Pytkowicz, R.M. and D.R. Kester, 1971, The physical chemistry of seawater, *Oceanogr. Mar. Biol. Ann. Rev.* 9, 11-60.

- Quinn, J.H., and N.C. Otto, 1971, Carbon dioxide exchange at the air-sea interface: Flux augmentation by chemical reaction, *J. Geophys. Res.* 76(6), 1539-1549.
- Redfield, A.C., 1948, The exchange of oxygen across the sea surface, *J. Mar. Res.* 7, 347-361.
- Revelle, R., and H. Suess, 1957, Carbon Dioxide Exchange Between Atmosphere and Ocean and the Question of an Increase of Atmospheric CO₂ during the Past Decades, *Tellus* 9(1), 18-27.
- Riley, J.P., and M. Tongudai, 1967, The major cation chlorinity ratios in seawater, *Chem. Geol.* 2, 263-269.
- Riley, J.P. and R. Chester, 1971, Introduction to Marine Chemistry, Academic Press, London and New York.
- SCEP, 1970, Man's Impact on the Global Environment, Cambridge, Mass., MIT Press, p. 320.
- Shishkina, D.V., 1964, Chemical composition of pore solutions in oceanic sediments, *Geochem. Inter.* 1(3), 522-528.
- Shulkin, M., and H.W. Marsh, 1962, Sound absorption in seawater, *J. Acoust. Soc. Am.* 34, 864-865.
- Sieburth, J.M., 1969, Studies on algal substance with seawater, III. The production of extracellular organic matter by littoral marine algal, *J. Exp. Mar. Biol. Ecol.* 3, 290-309.
- Siever, R., 1968, Establishment of equilibrium between clays and seawater, *Earth and Planetary Sci. Ltrs.* 5, 106-110.
- Sillén, L.G., 1961, The Physical Chemistry of Seawater, in: Oceanography, M. Sears, ed., AAAS publ. 67, pp. 549-581.
- Sillén, L.G., 1965a, Oxidation state of earth's ocean and atmosphere I, A model calculation on earlier states, The myth of the "probiotic soup," *Arkiv. Kemi.* 24, 431-456
- Sillén, L.G., 1965b, Oxidation state of earth's ocean and atmosphere II, The behavior of Fe, S and Mn in earlier states, Regulating mechanisms for O₂ and N₂, *Arkiv. Kemi.* 25, 159-176.
- Sillén, L.G., 1967a, How have seawater and air got their present compositions, *Chem in Britain* 3(7), 291-297.
- Sillén, L.G., 1967b, Master variables and activity, Scales, in: equilibrium Concepts in Natural Water Systems, Advances in Chemistry Series 67, ACS, Washington, D.C., pp. 41-69.
- Slowey, J.F., L.M. Jeffrey, and D.W. Hood, 1967, Evidence for organic complexed copper in seawater, *Nature* 214, 377-378.

Slowey, J.F., and D.W. Hood, 1971, Copper, manganese and zinc concentrations in Gulf of Mexico waters, *Geochim. Cosmochim. Acta* 35(2), 121-138.

Swinnerton, J.W., V.J. Linnenbom, and R.A. Lamontagne, 1970, The ocean: a natural source of carbon monoxide, *Science* 167, 984-986.

Stumm, W., and J.J. Morgan, 1970, Aquatic Chemistry, New York, Wiley-Interscience. 583 pp.

Teal, J.M., and J. Kanwisher, 1966, The use of PCO_2 for the calculation of biological production with examples from waters off Massachusetts, *J. Mar. Res.* 24(1), 4-14.

Thomas, W.H. and A.N. Dodson, 1972, Nitrogen deficiency in tropical pacific oceanic photoplankton II, Photosynthetic and cellular characteristics of a chemostat-grown diatom, *Limnol. Oceanog.* 17, 515-523.

Thompson, T.G., and K.H. Nelson, 1956, Concentration of brines and deposition of salts from seawater, *Am. J. Sci.* 2540, 227-239.

Thompson, G., and V.T. Bowen, 1969, Analyses of coccolith ooze from the deep tropical Atlantic, *J. Mar. Res.* 27(1), 32-38.

Thorp, W.H., 1965, Deep-ocean sound attenuation in the sub- and low-kilocycle-per-second region, *J. Acoust. Soc. Am.* 38, 648-654.

Turekian, K.K., 1969, The ocean, streams, and atmosphere, in: Handbook of Geochemistry, K.H. Wedepohl, exec. ed., Vol. 1, Berlin, Springer-Verlag, pp. 81-126.

Tzur, Y., 1971, Interstitial diffusion and advection of solute in accumulating sediments, *J. Geophys. Res.* 76(18), 4208-4211.

United Nations, 1968, Statistical yearbook, 1967, New York: Statistical Office of the United Nations.

Weyl, P.K., 1961, The carbonate saturometer, *J. Geol.* 69, pp. 32-44.

Wiere, W., 1930, Zur kenntnis der salze des Meereises, *Ann. d. Hydrography und Mar. Meteor. Jahrg.* 58, 282-286

Wilson, O.B., 1951, Technical Report No. IV. Dept. of Physics, UCLA, Contract No. N60NR-27507.

Wilson, W., 1960, Speed of sound in seawater as a function of temperature pressure and salinity, *J. Acoust. Soc. Am.* 32, 641-644.

Wollast, R., 1967, Kinetics of alteration of K-feldspar in buffered solutions at low temperature, *Geochim. et Cosmochim. Acta* 31, 635-648.

Wollast, R., 1973, The silica problem, in: The Sea, Vol. 5, E.D. Goldberg, ed., New York, Wiley (in press).

Wong, K.M., V.F. Hodge, and T.R. Folsom, 1972, Plutonium and polonium inside giant brown algae, *Nature* 237, 460-462.

Wyman, J., P.R. Scholander, G.A. Edwards, and L. Irving, 1952, On the stability of gas bubbles in seawater, *J. Mar. Res.* 11, 47-62.

Zirino, A., S.H. Lieberman, and M.L. Healy, 1972, *Proc. on Symp. on Mar. Electrochem.* Miami Beach, Florida (in press).

Zirino, A., and M.L. Healy, 1972, pH-controlled differential voltammetry of certain trace transition elements in natural waters, *Environ. Sci. and Technol.*, 6(3), 243-249.

Zlobin, V.S., and O.V. Mokuau, 1970, Mechanisms of the accumulation of plutonium-239 and polonium-210 by the brown algae *ascophyllum nodosum* and marine photoplankton, *Radiobiology* (translated by USAEC) X(4), 160-169.

PARTICIPANTS

Dr. Neil R. Andersen, Convener
Ocean Science and Technology Division
Office of Naval Research
Arlington, VA 22217

Dr. Gordon Atkinson
Department of Chemistry
University of Oklahoma
Norman, OK 73069

Dr. Max Blumer
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Dr. James H. Carpenter
Oceanography Section, Room 317
National Science Foundation
1800 G Street, N.W.
Washington, DC 20550

Dr. Keith E. Chave
Department of Oceanography
University of Hawaii
Honolulu, HI 96855

Dr. Harmon Craig
Scripps Institution of Oceanography
University of California, San Diego
La Jolla, CA 92037

Dr. Werner G. Deuser
Woods Hole Oceanographic Institution
Woods Hole, MA 02540

Dr. John M. Edmond
Department of Earth & Planetary Science
Massachusetts Institute of Technology
Cambridge, MA 02139

Dr. Frederick H. Fisher
University of California, San Diego
P.O. Box 109
La Jolla, CA 92037

Dr. Theodore R. Folsom
Scripps Institution of Oceanography
University of California, San Diego
La Jolla, CA 92037

Dr. Edward D. Goldberg,
Discussion Leader
Chemical Fluxes Through the Marine
Environment, Including Air-Sea and
Sediment-Sea Exchanges
Scripps Institution of Oceanography
University of California, San Diego
La Jolla, CA 92037

Dr. Louis I. Gordon
School of Oceanography
Oregon State University
Corvallis, OR 97331

Dr. Michael L. Healy
Department of Oceanography
University of Washington
Seattle, WA 98105

Dr. Donald W. Hood
Institute of Marine Sciences
University of Alaska
College, AK 99735

Dr. David C. Hurd
Department of Oceanography
University of Hawaii
Honolulu, HI 96855

Dr. John M. Hunt
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Dr. Lela M. Jeffrey
Department of Oceanography
Texas A & M University
College Station, TX 77843

Mr. John J. Kelley
Institute of Marine Sciences
University of Alaska
College, AK 99701

Dr. Dana R. Kester
Narragansett Marine Laboratory
University of Rhode Island
Kingston, RI 02881

Dr. Patrick Kinney
Institute of Marine Sciences
University of Alaska
College, AK 99701

Dr. Lawrence H. Larsen
Oceanography Section, Room 317
National Science Foundation
1800 G Street, N.W.
Washington, DC 20550

Dr. Frank J. Millero, Discussion Leader,
Processes and Mechanisms Governing the
Inorganic Composition of Seawater
Institute of Marine and
Atmospheric Sciences

University of Miami
Miami, FL 33149

Dr. Theodore T. Packard
Department of Oceanography
University of Washington
Seattle, WA 98105

Dr. Patrick L. Parker
International Decade for Ocean
Exploration, Room 710
National Science Foundation
1800 G Street, N.W.
Washington, DC 20550

Dr. Bobby J. Presley
Department of Oceanography
Texas A & M University
College Station, TX 77843

Dr. Charles Culberson
School of Oceanography
Oregon State University
Corvallis, OR 97331

Dr. Francis A. Richards,
Discussion Leader,
Impact of Life Processes on the
Chemistry of the Oceans
Department of Oceanography
University of Washington
Seattle, WA 98105

Dr. William M. Sackett
Department of Oceanography
Texas A & M University
College Station, TX 77843

Dr. David R. Schink
Department of Oceanography
Texas A & M University
College Station, TX 77843

Dr. Robert E. Stevenson
Office of Naval Research
Scripps Institution of Oceanography
La Jolla, CA 92037

Dr. Eugene D. Traganza
Department of Oceanography
Naval Postgraduate School
Monterey, CA 93940

Dr. Karl K. Turekian
Department of Geology and Geophysics
Yale University
New Haven, CT 06520

